On the theory of transient hot-wire measurement of the thermal conductivity of electrolytic solutions

Baruël, P.

Publication date:
1973

Document Version
Publisher's PDF, also known as Version of record

Risø Report No. 280

Risø Report No. 280

Danish Atomic Energy Commission

Research Establishment Risø

On the Theory of Transient Hot-Wire Measurement of the Thermal Conductivity of Electrolytic Solutions

by Pierre Baruël

January 1973

Sales distributors: Jul. Gjellerup, 87, Sølvgade, DK-1307 Copenhagen K, Denmark
Available on exchange from: Library, Danish Atomic Energy Commission, Risø, DK-4000 Roskilde, Denmark

UDC 536.2.08: 541.135.2

January 1973 Risø Report No. 280

On the Theory of Transient Hot-Wire Measurement of the Thermal Conductivity of Electrolytic Solutions

by

Pierre Baruël

Danish Atomic Energy Commission
Research Establishment Risø
Engineering Department

Abstract

In two previous works [2] and [3] the author has presented some investigations concerning measurement of the thermal conductivity of liquids by the transient hot-wire method. The "classical" field of application of this method is pure, dielectric liquids.

In [3] was described a modification - worked out by the author - of the method to apply also to electrolytic solutions. In that modification the electrically insulating layer round the hot wire used - or proposed - by other authors for electrolytic measurements is avoided. The layer gives rise to practical and theoretical difficulties.

For practical reasons it was necessary to limit in [3] the discussion of the underlying theory and mainly present the experiments. The purpose of the present work is to go more thoroughly into the theoretical foundation of the modification so that its underlying idea and sources of error can be understood and estimated better.

If one applies a voltage below the decomposition voltage of an electrolytic solution to the electrodes of a simple electrolysis system containing the solution, a pulse of current will pass through the liquid. The (non-linear) differential equation for the development in time of pulses of the simplest

type is derived. Current pulses also occur in the modified apparatus and if the effect of them does not fade out sufficiently fast they disturb the registrations during the measurement. The said equation is generalized to comprise the actual, more complicated apparatus, and on this basis a theoretical justification and explanation of the author's modification - i.e. of the contents of [3] - is set forth.

In the last section the importance with regard to measurements of the ambiguity of the concept of thermal conductivity of mixtures owing to the so-called "cross-effects" is briefly discussed.

The reason why the report is a little lengthy is, among other things, that an attempt has been made to make it a self-contained work, readable also to a researcher who is e.g. an expert in heat transmission, but less familiar with electrode kinetics. (The author himself is not an expert in the last-mentioned field, but has had to study it to some extent). Subsections II a and II b may be skipped by a reader familiar with electrode kinetics.

The apparatus described in [3] was only developed to a semiautomatic stage. Now full automation has been introduced and a more comprehensive set of measurements has been carried out with very favourable results. The main purpose of the present report is to serve as a foundation to which can be referred in a final report containing a compact survey of the author's theoretical investigations on the method and giving the new measurements.

ISBN 87 550 0179 3

CONTENTS

1. Purpose and Contents of the Investigation

The present work is a continuation of two earlier works [2] and [3] concerning the transient hot-wire method for determination of the thermal conductivity λ of liquids.

As is well known, the principle of this method is as follows. The liquid is filled into a cylindric cell vertically placed in a thermostat. Along the axis of the cell a hot wire is located. When an electric current is fed into a circuit of which the cell is a component, heat will flow from the wire into the liquid. The better the liquid conducts the heat away from the wire, the more slowly the wire temperature increases. In addition to its function as a source of heat, the wire therefore acts, in most designs, as a resistance thermometer, which makes it possible to register its temperature versus time curve by means of a recorder built into the circuit. The wire temperature can also be measured by means of a thermocouple. From the curve registered, and from certain other measurements in the system, the thermal conductivity of the liquid can be deduced according to the theory of the method.

In [2] was treated some aspects of the theory of the method, when it is used for λ-measurements on pure dielectric liquids, which is its "classical" field of application. In [3] was treated a modification of the method - worked out by the author - to comprise also electrolytic solutions.

In spite of the fact that certain advantages are often claimed for the method, such as those of being "elegant", fast, and convenient, amazingly few attempts have been made to expand it for measurements on electrolytic solutions since it was introduced in 1931 by Stålhane and Pyk [13] and refined in 1938 by Eucken and Englert [7]. 'Attempts at expansion' are here taken to mean: actually presented works on the theory and practice of such an expansion. A suggestion for the accomplishment of this expansion is often found in the literature, namely: the hot wire should be surrounded with an electrically insulating coating. The only two actually presented works known to the author on the expansion of the transient hot-wire method to comprise also electrolytes, namely one by van der Held and van Drunen [16] from 1949 and one by Alas [1] from 1967, are also built upon this idea. It can presumably be established that in the literature it has till now been taken for granted that use of an electrically insulating layer is the only possibility of expansion *). Thus van der Held and van Drunen say in their above-mentioned work from 1949 (page 868):

*) The present author knows of no exceptions.

"Not only the chemical activity of some liquids but also phenomena like polarisation and electrophorese made it impossible to use the bare wire in the liquid."

In his 1967-work, page 12, Alas says that "die Forderung nach einer Schutzschicht" is "selbstverständlich". In another connection Alas also quotes a work by Bryngdahl in which electrical insulation is stated to be the only possible solution. (Bryngdahl only mentions the possibility of electrolyte measurements by the method but does not perform any work on such measurements.)

As for the two actually presented works [1] and [16] that use an electrically insulating layer, [16] was revoked by van der Held in co-operation with Hardebol and Kalshoven in 1953 [17], and in [1] (1967) Alas found it necessary to use a very thin layer of a material that is dissolved by bases. According to Alas's express statement this means that measurements on bases cannot be made - even though one might imagine that the short duration of the measurements nevertheless made measurements on bases possible if the layer is changed sufficiently often.

In [3] it was demonstrated by the present author that cell and circuit can be modified so that measurements can be made on a very comprehensive range of bases, salts and acids without the introduction of an electrically insulating layer round the hot wire. The idea of omitting the electrical insulation round the hot wire arose from a feeling that this insulation will give rise to difficulties - which was later confirmed in several ways through Alas's work - and from an intuitive idea that the electrolytical polarization may be considered as a counter electromotive force which it must be possible to make balance with the voltage applied to the cell. The electric current will then automatically be barred from passing through the liquid. If this can be obtained sufficiently fast, the cell with the electrolytic solution can be considered as if the liquid were dielectric for a sufficiently long period for measuring without complications.

The author has now improved the technical aspects of his originally semi-automatic set-up by making it fully automatic, and a more comprehensive set of measurements has been carried out. The results arrived at have been very favourable, and if possible they will be described in a final report.

As to the discussion of the theoretical aspects, it was for practical reasons intentionally limited in [3]. That work mainly describes the experiments carried out, before the full automation was introduced, for the purpose of confirming the applicability of the modification. But in [3] it

frequently turns out that it would be desirable to treat the theory of the modification more thoroughly in another work because the whole treatment of the readings - i.e. the combination of them for the computation of λ and the interpretation of the so-called "blank experiments" (cf. [3], page 18) - can of course only be carried out according to an underlying theory.

Briefly, it is therefore the purpose of the present work to give a more elaborate theoretical foundation and explanation of the modification.

The "balance" between applied voltage and counter electromotive force is not obtained instantaneously. A current pulse will pass through the liquid, and registrations cannot be made before this pulse has faded out. Incidentally - as indicated in [3] - this also holds true if an insulating layer round the wire is used, as it is more clearly seen from the present work.

As the measurement proceeds according to the "classical" theory of the method after the passing off of the current pulse, the desired theoretical foundation of the modification is centered round the development in time of such current pulses. The present work is therefore chiefly a theoretical investigation of this problem, which does not seem to be treated - in other connections - in the literature, at least not in a way so that the results needed here can be found. The importance of the development in time of the current pulse - which disturbs the electrical registrations - stems among other things from the problem of convection. The fading out of the pulse must be sufficiently fast, because there must be time enough to make a sufficient set of registrations without electrical disturbances before the convection in the cell becomes turbulent and disturbs the heat transport.

As mentioned in the abstract the present work is a little lengthy in order to make it readable to a researcher interested in λ-measurement but less familiar with electrode kinetics. The present author is not an expert in the last-mentioned field but has had to study it to some extent.

It should be emphasized that the present work and the theoretical part of [2] is by no means intended to be a general theoretical contribution to the treatment of heat conduction in liquids. The work only concerns the theory of measurement of λ (by the method). The measurements described in [3] were mainly carried out to confirm experimentally - by comparison with λ-values found in the literature and obtained by other methods - the applicability of the modified method to electrolytic solutions. It has not been within the scope of the work to give a general theoretical discussion of the results obtained or of energy transport in liquids in general.

Nowadays a treatment of the latter subject and a discussion of the measured λ-values in [3] would certainly require microphysical-statistical considerations. But for the purpose of the present and the previous works, [2] and [3],macrophysical theory (i.e. modern non-equilibrium thermodynamics) is deemed fully adequate. Although it is pointed out that a certain quantum-statistical phenomenon ("tunneling") may in principle play a role. the author feels that it would be out of proportions to try to give a quantum physical treatment. The tunnel effect is presumably of minor importance in the present connection.

How intensively work on development of methods for λ-measurement is nowadays cultivated is seen e.g. from the publication of the composite 2-volume work [15] from 1969. True, this work contains a chapter on statistical theory of heat conduction, but this is only meant to give a general introduction. All the different measurement methods and their sources of error are treated by macrophysical theory in the said composite work [15].

Two distinctions constantly used in the following must be mentioned here. The first is of general theoretical importance. The second has only bearings on the actual work presented in [3] and in the present report.

The first distinction is that between "non-faradayan" and "faradayan" current pulses in an electrolysis system in which the applied voltage is below the decomposition voltage of the electrolyte. The second distinction is a distinction between "blank experiments" and "main experiments" In [3] 'main experiments' is used synonymously with 'measurement of λ'.

The author does not know if the words 'faradayan pulse' and 'non-faradayan pulse' are commonly used. But they*) are used in an older booklet by Thon [14] on electrolytic polarization phenomena. The distinction "faradayan - non faradayan" is explained in [3], page 18 f. Here we may explain this distinction by quoting Thon loc cit. Thon describes his situation as follows:

"Donc, nous avons deux électrodes et un électrolyte quelconques et nous appliquons, de source extérieure, une tension électrique, d'abord faible, entre les deux électrodes."

Thon thus applies a small voltage to the electrodes. That the voltage is small means that it is below the decomposition voltage of the electrolyte. Having mentioned that the applied voltage causes transport of ions to the electrodes where the ions make up parts of the interfacial layers, boardering to charges of opposite sign in the metal part of these layers, he continues, considering one of the electrodes:

"Un courant a passé de l'électrolyte, à travers l'électrode, dans le circuit extérieur - mais y a-t il eu électrolyse? Non pas .... Ici aucun ion ne s'est déchargé, il n'y a pas de produits d'électrolyse électriquement neutres. Le courant a servi uniquement à charger le condensateur élémentaire qu'est l'électrode. La loi de Faraday ne s'appliquant pas à ce courant de charge, nous dirons que ce courant est non-faradique."

A little later Thon speaks about "l'action du courant momentané" which is said to be the result of applying a small voltage. The phenomenon could hardly be described more clearly: Quite generally arbitrary electrolytic solutions are considered under the influence of "small" voltages. The process in the electrolytic solution is then, according to Thon, simply an instantaneous "non-faradayan" pulse of ion transports through the solution to and from the interfacial layers, and nothing more happens if one does not increase the applied voltage:

"Une fois la polarisation**) des électrodes devenue égale à la tension appliquée, le courant s'arrête, car il n'y a plus de tension disponible pour une chute ohmique."

Now it is certainly an exaggeration to say that the pulse is always "instantaneous". But Thon's essay is purely qualitative and therefore, in his context, it does no harm to consider the pulse faded out instantaneously. If Thon's dictum could be taken literally - i.e. if general theoretical investigations showed that, below the decomposition voltage, the pulse could

---

*) At any rate the last mentioned: 'non-faradique'

**) Thon has chosen the abbreviation 'polarisation' for 'la tension de polarisation'.

only be described as a mathematical singularity in time - there would be no further problems. But a glance at fig. 11 of [3] - reproduced here as fig. 4, page 27 - at which such a pulse is indirectly registered in an unmodified, "classical" set-up shows that this is not so. It even turns out in section IV of the present report that the registered pulse cannot have been of the "non-faradayan" type.

There is no doubt that each current pulse in an electrolytic solution (below the decomposition voltage) must be non-faradayan at the outset, ions and electrons being transported to and from the interfacial layers between the electrodes and the solution. But these transports may very well cause, as a "secondary effect", the formation of what will later be termed 'reaction zones' in the layers in which displacements of possible chemical reactions may then take place. Such "secondary effects" may delay the fading out of the pulse. They will even prevent the process from ending in a thermodynamically stable equilibrium. As we are operating below the decomposition voltage, there will be no formation of new chemical phases, but neutral products formed in the interfacial layers will begin to diffuse out in the bulk of the solution. Thus, strictly speaking, the process will continue slowly although in practice one may consider the result of the process as if a state of partial equilibrium has been obtained. A pulse passing off according to this pattern is what is termed 'a faradayan pulse' in the present work.

One might expect all pulses of the kind considered here to be faradayan, the non-faradayan pulses being only idealized limiting cases. But it should be borne in mind that electrode kinetics is a very complicated field, and that many more or less predictable phenomena - like "overvoltage" - may play a role. Such phenomena may alter the result. As a matter of fact non-faradayan polarization is more than an "academic" abstraction. It does occur, which can be seen from more modern and more quantitative treatises than that of Thon as e.g. that of Delahay [6].

It might be a little more up-to-date to use the term 'ideal polarization' instead of 'non-faradayan polarization'. From Delahay [6], page 17, we quote:

"A number of electrodes can function as ideal polarized electrodes, and conditions are particularly favourable for mercury in aqueous solution ..... The range of potentials that can be covered with other metals is somewhat narrower than for mercury."

The second distinction used throughout the present work is that of "blank experiments" versus "main experiments".

From section IV it will be seen that - under the presumptions of the present work - non-faradayan pulses will not cause disturbances. But the author has had no opportunity to investigate in detail whether it would be possible to study also "faradayan complications" in general and to find reasonable limits for the delaying effects of these.

Before using the modification one must therefore have some trustworthy experimental indication that such a delay does not occur to such an extent that it disturbs the registrations. Such indication is furnished by the "blank experiment" technique described in [3], section III. Briefly, the idea of this technique is to replace the platinum hot wire by a manganin wire with the same resistance and to make registrations through a period as long as that used for the "main experiments", i.e. the measurements. As the temperature-resistance coefficient of manganin is extremely small, only disturbances, if any, from the current pulse will be registered during such a "blank experiment".

The theoretical foundation of the investigation is set forth in section II, which contains nothing original. That section mainly serves the purpose to collect the necessary, well known formulae for later reference and to mention the used "models" of the interfacial layers. Subsections II a and II b may therefore be skipped by a reader that is familiar with electrode kinetics.

The purpose of the last section of the present work is to round off the work on λ-measurement of liquids presented in [2], [3] and the present work. The underlying, general theory of such measurements has by the author only been treated in [2] for the case of pure dielectric liquids (loc cit page 9, f.). The problem treated in the said section of the present work is the following. For pure dielectric liquids λ may be considered defined by "Fourier's law"

$$\vec{j}_u = -\lambda \operatorname{grad} T \ ,$$

where $\vec{j}_u$ is the density of the diffusion flow of non-mechanical energy ("heat"), and T is the temperature. But - at least since Onsager presented his famous theory - it has been a well-known fact that if one proceeds from pure substances to mixtures, there will generally occur some "cross-effects" between the diffusion flows of the components and of energy. This is valid for both dielectric and electrolytic mixtures. If e.g. one considers a dielectric, binary mixture one must replace Fourier's law with an expression of the form

$$\vec{j}_u = \alpha \operatorname{grad} T + \beta \operatorname{grad} \mu ,$$

where α and β are "phenomenological coefficients" and μ is the chemical potential of one of the components. So - in principle - one may now ask: what is meant by speaking about the thermal conductivity of a binary mixture. As is well known the concept 'thermal conductivity' now becomes ambiguous: If e.g. $\operatorname{grad}\mu = \vec{0}$ one has "a Fourier law" of the form

$$\vec{j}_u = \alpha \operatorname{grad} T$$

and if e.g. $\mu = \mu(T)$, as will be the case at constant pressure if there are no chemical reactions in the liquid, one has "a Fourier law" of the form

$$\vec{j}_u = (\alpha + \beta \frac{d\mu}{dT}) \operatorname{grad} T$$

This ambiguity is never mentioned in the literature on measurement on mixtures and, true, it should not be exaggerated. But - as demonstrated in the last section - if it is not negligible, different devices may give different results. Anticipating it can be said that for gaseous mixtures there must be such cases in which the ambiguity cannot be ignored (and the method is as important for gaseous "materials" as for liquid*) ones). As to liquid mixtures - at least dielectric ones - it is found that the ambiguity of λ is - apart from certain possible exceptions - completely insignificant. As the whole theoretical foundation is much more complicated for fluid mixtures than for pure liquids this can hardly be said to be self-evident.

---

*) The method may even be used for solid materials by melting them down into the cell and letting them solidify round the wire.

II. The Theoretical Foundation of the Investigation

a. Formulae and Presumptions

In this subsection some formulae from non-equilibrium thermodynamics that will be used in the investigation are collected. Some assumptions which must be made in order to eliminate inessential details are mentioned, and finally is derived an expression needed later on.

The writing down of the formulae only serves the purpose of providing a list for later reference. This list comprises nothing original and as said in the abstract, subsections II a and II b may be skipped by a reader familiar with electrode kinetics.

First and foremost the Maxwell equations must be applied. They read

$$\left.\begin{aligned} \operatorname{curl} \vec{E} + \frac{\partial \vec{B}}{\partial t} &= \vec{0} \\ \operatorname{curl} \vec{H} = \vec{i} + \frac{\partial \vec{D}}{\partial t} & \\ \operatorname{div} \vec{D} &= \rho \\ \operatorname{div} \vec{B} &= 0 \quad . \end{aligned}\right\} \qquad (1)$$

where

t = time

$\vec{E}$ = electric field

$\vec{D}$ = electric induction

$\vec{B}$ = magnetic induction

$\vec{H}$ = magnetic field

$\vec{i}$ = electric current density

ρ = electric charge density

The vector operators refer to space coordinates in a coordinate system in which the system considered is at rest. From the equations it immediately follows that $\vec{E}$ can always be written on the form

$$\vec{E} = -\operatorname{grad} \varphi - \frac{\partial \vec{A}}{\partial t} \quad , \qquad (2)$$

φ being the scalar potential and $\vec{A}$ the vector potential.

The equations (1) must be supplemented by "constitutive" equations whereby the chemical nature of the system is taken into account. Let ε = the dielectric tensor and μ = the magnetic permeability tensor. We then have

$$\left.\begin{aligned} \vec{D} &= \varepsilon \cdot \vec{E} \\ \vec{B} &= \mu \cdot \vec{H} \end{aligned}\right\} . \qquad (3)$$

ε and μ are dependent on the intensive properties of the system, and they reduce to scalars provided the system is isotropic. This presumption will be taken as fulfilled.

The magnetic field around the wire is strictly speaking an external magnetic field to the liquid producing some small effects in it which cannot be taken into account through constitutive equations for isotropic materials. For example the Hall effect is neglected by the presumption of isotropy. As to the mechanical aspects this presumption means that interfacial tension is ignored.

Non-equilibrium thermodynamics now provides us with further constitutive equations also taking a simple form. Into these equations enter so-called "phenomenological coefficients" that reduce from tensors to scalars when the system is isotropic. These equations give the flow densities for the chemical components and for energy ("heat") or entropy as linear combinations of certain "forces" or "force densities", the phenomenological coefficients being the coefficients of the linear combinations. The coefficients are dependent on the intensive properties of the system but they are not - as are the forces - dependent on derivatives of these properties with respect to the space coordinates.

Strictly speaking we ought to have said 'diffusion flow densities' instead of 'flow densities' because, if the system is not in a state of mechanical equilibrium, convective contributions must be added to the said linear combinations to give the total flow densities. However, in the present work it will be assumed that the condition of mechanical equilibrium is (very nearly) satisfied because one may delimit the time in which the system is considered to e.g. a second after the current to the cell is switched on. Then, in accordance with the investigations on the convection in the system in [2], section III it will be a reasonable assumption that convection may be neglected for the present purpose.

If there are n components - charged or uncharged - one has n equations for their mass flow densities. L_{kr} and γ_k being (scalar) phenomenological coefficients and $\vec{j}_k$ being the mass flow density of component k these equations read

$$\vec{j}_k = \sum_{r=1}^{n} L_{kr} \vec{K}_r + \gamma_k \operatorname{grad} T, \qquad k = 1, 2 \ldots n \ , \qquad (4)$$

where T = temperature and $\vec{K}_r$ is the r^{th} force density.

(4) can be expanded with an equation for energy- or entropy flow and one will then still have as many equations as there are flow densities (and forces), namely n + 1. But in the following this last equation will not play a role until during the considerations in the last section.

The $\vec{j}_k$'s are, as is well known, defined in such a way that their sum is $= \vec{0}$ (cf. section V, page 69). Accordingly, the equations (4) are not independent and one of them is "superfluous". It can be seen *) that, if e.g. the equation for $\vec{j}_n$ is left out of consideration, the system of equations may be written in the form

$$\vec{j}_k = \sum_{r=1}^{n-1} L_{kr} (\vec{K}_r - \vec{K}_n) + \gamma_k \operatorname{grad} T, \qquad k = 1, \ldots n - 1 \ , \qquad (5)$$

the L_{kr}'s now being new phenonenological coefficients.

In (4) and (5) the $\vec{j}_k$'s are, as said, mass flow densities. If the equation for $\vec{j}_k$ is multiplied by the charge pr. unit mass of component k and all the equations are added, one has for the total electric current density $\vec{i}$ an expression of the form

$$\vec{i} = \sum_{k=1}^{n-1} \sum_{r=1}^{n-1} \alpha_{kr} (\vec{K}_r - \vec{K}_n) + \Gamma \operatorname{grad} T \ , \qquad (6)$$

provided that component n is neutral (it may for instance be H_2O).

If the expressions for the $\vec{K}$'s are now given, the necessary formulae have been collected. These expressions (see e.g. [5] , page 344 where they enter the expression for the entropy production density **) are

$$\vec{K}_i = (z_i \vec{E} - \operatorname{grad} \mu_i) \frac{1}{T} \ , \qquad (7)$$

where

---

*) See e.g. Haase [9], page 110

**) In [5], page 344, formula (40) we must, according to our presumption mentioned above, put $\vec{v} = \vec{0}$.

μ_i = chemical potential of component i defined by reference to the mass unit and not, as is usual in chemistry, to 1 mole.

z_i = charge pr. unit mass of component i

T = temperature

If (7) is substituted into (6) one finds an equation which - using a denotation that is a little loose but easily comprehensible - may be written

$$\vec{i} = \sigma \vec{E} + \Sigma A \operatorname{grad}\mu + \Gamma \operatorname{grad} T \quad , \tag{8}$$

where σ, Γ and the A's are functions of pressure p, temperature T and x_1, $x_2 \ldots$ = the mole fractions of the components. The same holds good for the μ's:

$$d\mu = \frac{\partial \mu}{\partial p} dp + \frac{\partial \mu}{\partial T} dT + \sum \frac{\partial \mu}{\partial x} dx \quad ,$$

and (8) may therefore also be written on the form

$$\vec{i} = \sigma \vec{E} + \pi \operatorname{grad} p + \Sigma A^* \operatorname{grad} x + \Gamma^* \operatorname{grad} T \quad . \tag{9}$$

If finally (2) is used a strongly generalized form of Ohm's law on differential form is found:

$$\vec{i} = -\sigma \operatorname{grad} \varphi - \sigma \frac{\partial \vec{A}}{\partial t} + \pi \operatorname{grad} p + \Sigma A^* \operatorname{grad} x + \Gamma^* \operatorname{grad} T \quad . \tag{10}$$

The only presumptions for the validity of this equation are isotropy and mechanical equilibrium. All terms on the right-hand side but the first may be said to represent electromotive forces (or electromotive force densities) after division by σ.

In the following the bulk phases of the system will be termed 'the macrophases' and the interfacial layers 'the microphases'. In the first mentioned phases the condition of mechanical equilibrium is *)

$$\operatorname{grad} p = \vec{0} \quad ,$$

owing to the requirement of electroneutrality. If the microphases are - as they will be later - considered steep but continuous transition zones (or rather composed of such zones) the mechanical equilibrium condition is in these phases

*) Here we have ignored the gravitational field.

$\operatorname{grad} p = \rho \vec{E}$,
(ρ = electric charge density)

Therefore, we can for macro- as well as for microphases according to our presumptions write (9) as

$$\vec{i} = \sigma \vec{E} + \Sigma A^* \operatorname{grad} x + \Gamma^* \operatorname{grad} T \quad , \tag{11}$$

and (10) as

$$\vec{i} = -\sigma \operatorname{grad} \varphi - \sigma \frac{\partial \vec{A}}{\partial t} + \Sigma A^* \operatorname{grad} x + \Gamma^* \operatorname{grad} T \quad , \tag{11a}$$

where, strictly speaking, 'σ' now ought to be replaced by another symbol.

To avoid complications it is assumed in the following that the thermoelectric contribution $\Gamma^* \operatorname{grad} T$ to the total electromotive force (density) is negligible. So if one puts

$$\Sigma A^* \operatorname{grad} \vec{x} = \vec{\mathcal{E}} \quad ,$$

one has

$$\vec{i} = \sigma \vec{E} + \vec{\mathcal{E}} \quad ,$$

or

$$\left.\begin{aligned} \vec{i} &= -\sigma \operatorname{grad} \varphi - \sigma \frac{\partial \vec{A}}{\partial t} + \vec{\mathcal{E}} \\ \vec{\mathcal{E}} &= \Sigma A^* \operatorname{grad} x \quad , \end{aligned}\right\} \tag{12}$$

Finally we shall in this subsection derive a result that will be needed later on. If we ignore the "thermoelectric terms" in the system of equations (5), they read

$$\vec{j}_k = \sum_{r=1}^{n-1} L_{kr} (\vec{K}_r - \vec{K}_n), \qquad k = 1, \ldots n-1,$$

and if they are considered a system of n - 1 equations for the n - 1 $(\vec{K}_r - \vec{K}_n)$'s they can be solved according to Cramer's rule. The determinant L made up of the L_{kr}'s is according to non-equilibrium thermodynamics $\neq 0$. One finds

$$\vec{K}_r - \vec{K}_n = \frac{1}{L} \sum_{s=1}^{n-1} A_{rs} \vec{j}_s \quad ,$$

where the A_{rs}'s are minors taken with the right sign. If this result is combined with (7) one finds

$$\left.\begin{aligned} &\text{grad}\,(\mu_r - \mu_n) - (z_r - z_n)\,\vec{E} = -\frac{T}{L}\sum_{s=1}^{n-1} A_{rs}\,\vec{j}_s \\ &(z_n = 0)\ . \end{aligned}\right\}$$

If an aqueous solution is considered, H_2O may be taken as component n. Thus

$$\text{grad}\,(\mu_r - \mu_{H_2O}) - z_r\,\vec{E} = \Sigma\, B_{..}\,\vec{j}_{.}\ ,$$

where the summation indices have been dropped and T is included in the coefficients of the $\vec{j}$'s. The indices of the symbols have been replaced by dots.

For the sake of convenience we now change to the more "chemical mode of writing" by multiplying this equation with the mole weight M_r of component r and we will change the denotation of 'μ_r' to be $M_r\mu_r$. The result is

$$\text{grad}\,(\mu_r - M_r\mu_{H_2O}) - z^*_r F\,\vec{E} = \Sigma\, B^*_{..}\,\vec{j}_{.} \quad , \tag{13}$$

where Fz^*_r = charge per mole of component r and F = 96500 coulomb, z^* being the electrovalency. The meaning of the $B^*_{..}$'s is obvious.

In order to carry through the calculations - which are merely meant as an investigation of the order of magnitude of the time within which the non-faradayan pulses of current can be expected to fade out - the foundation will be idealized and it will be assumed that the laws of diluted solutions hold good in both macro- and microphases. In other words we put

$$\mu_r = R\,T\,\ln x_r + \text{const}\ , \tag{14}$$

where R = the gas constant. Furthermore x_{H_2O} and the activity coefficient of water are considered to be nearly constant also in the microphases. One thus has

$$\mu_{H_2O} = \text{const}\ . \tag{14a}$$

In (14) and (14a) the terms 'const' stand, strictly speaking, for functions of T and p. As only small temperature differences - which will be ignored - occur in the system and since what is needed later is an integration of (13) "through" microphases, which are extremely "thin", it must be considered reasonable to leave out grad μ_{H_2O} in (13) for the present purpose. One thus ends up with

$$\text{grad } \mu_r - z_r^* F \vec{E} = \Sigma B_{..}^* \vec{j}_{.} \quad , \tag{15}$$

which will be used later.

b. On the Structure of the Interfacial Layers (the Microphases)

In the appendix of [3] a very simple "derivation" of the passing off of the current pulses was mentioned, but it was pointed out that this "derivation" is unreliable, for instance was mentioned an erroneous consequence of it. The present work clearly demonstrates that it does not hold good and that the passing off of the current pulses are generally much slower.

The reason why this "derivation" - the result of which can only asymptotically describe the very last period of the fading out - was mentioned is that to a certain degree the "derivation" is in accordance with reasoning which can be found in the literature, as will be mentioned shortly. As the "derivation" is very simple, it is also rather convincing and unsophisticatedly one may be inclined to think it is reliable. But it was emphasized that this is not so.

The result of the "derivation" is that the $\vec{i}$ field in the microphases fulfils the equation

$$\frac{\partial}{\partial t}\left(\vec{i} + \frac{\varepsilon}{\sigma}\frac{\partial \vec{i}}{\partial t}\right) - \vec{0} \quad , \text{ where } \begin{cases} \varepsilon = \text{the dielectric permeability} \\ \mu = \text{the magnetic permeability} \\ \sigma = \text{the specific conductivity} \end{cases} \tag{16}$$

$\frac{\varepsilon}{\sigma}$ is of the order of magnitude*) of 10^{-10}s (see [3], appendix). It would be very fortunate if (16) were reliable: integrating one finds that the pulse should fade out exponentially with a time constant of about 10^{-10}s. Therefore in the present context, the pulses might be said to have faded out "instantaneously" quite independent of the design of the cell and the circuit and of the nature of the pulses i.e. whether they are "non-faradayan" or not. However the result (16) and its integrated form

$$\vec{i} = \vec{i}_0 \, e^{-\frac{\sigma}{\varepsilon}t} \simeq \vec{i}_0 \, e^{-10^{10}t}, \tag{16a}$$

*) This is valid e.g. for a 1 N aqueous KCl solution

$\vec{i}_0$ being the initial field, is obtained from (1) by putting $\vec{E} = -\text{grad}\varphi$ and $\vec{i} = \sigma\vec{E} = -\sigma\,\text{grad}\varphi$ which generally cannot be correct according to (2) and (11a) or (12). In the macrophases we have quite correctly $\vec{\mathcal{E}} = \vec{0}$ in (12), because there are no x-gradients, but it is erroneous to put $\frac{\partial\vec{A}}{\partial t} = \vec{0}$ during so fast a process as that described by (16a). Strictly speaking one must have $\vec{i}_0 = \vec{0}$, $\text{grad}\varphi$ being "balanced" at the outset by $\frac{\partial\vec{A}}{\partial t}$. The last mentioned quantity must therefore, at any rate during the first stages of the process, when $|\vec{i}|$ increases, be of the same order of magnitude as $\text{grad}\,\varphi$. (16a) may therefore at best be an approximation corresponding to an extremely steep increase of $|\vec{i}|$ which, according to the said equation, must reach $|\vec{i}_0|$ instantaneously. As the decrease from $|\vec{i}_0|$ is also extremely fast at the outset we cannot either put $\frac{\partial\vec{A}}{\partial t} = \vec{0}$ during the first stages of the decrease. In other words: we cannot a priori put $\frac{\partial\vec{A}}{\partial t} = \vec{0}$ and write $\vec{i} = -\sigma\,\text{grad}\varphi$ although similar calculations can be found in the literature where this is done. In the well known book [10] by Harned and Owen one finds e.g. on page 94 an equally fast phenomenon treated by using "Ohm's law $\vec{i} = -\sigma\,\text{grad}\varphi$", and this is the reason why the "result" (16a) has been mentioned here. One might, by referring to, e.g., the said book point out to the present author, that the problem must be quite elementary and perhaps, that it is solved by (16a).

The problem treated by Harned and Owen loc. cit is the following. If we (instantaneously) distribute charge with density ρ_0 in an homogeneous, electrically conductive phase, how long will it be before electroneutrality is re-established. The result is quite analogous to (16a), namely

$$\rho = \rho_0 e^{-\frac{\sigma}{\varepsilon}t} \quad , \tag{17}$$

It should be emphasized that the present author by no means doubts this result, but only the very derivation, using the equation $\vec{i} = -\sigma\,\text{grad}\,\varphi$. For our problem this equation is completely inadequate. Incidentally (16) may equally easily be obtained without using the said equation as it is correctly done e.g. by Born [4], page 611-612. (17) might by some kind of "common sense analogy" be felt to support the wrong result (16a), but the current pulses have nothing to do with the disappearance of space charges in macrophases. Seen from a macroscopical point of view the macrophases are electroneutral, and the pulses are processes of transport of charge between microphases or parts of these. Such transport may very well take place through the neutral macrophases ($\rho = 0$), because both positive and negative ions flowing in opposite directions participate.

It is easy from (1) to derive a correct expression for the $\vec{i}$ field being valid in the macrophases where ε, μ and σ are constants owing to the homogeneity (and to $\text{grad}\,T \simeq \vec{0}$). As is well known the result is an equation of damped $\vec{i}$ - waves. But trying to confine the considerations to the macrophases one will find it difficult to prescribe reasonable initial and boundary conditions for this equation. In other words: the only way to treat the problem is to make a circuit analysis taking into consideration the state of things in the microphases - which one "passes through" scanning the circuit. It is therefore necessary to consider more closely the microphases.

In modern standard treatises on non-equilibrium thermodynamics such as e.g. [5], [9] and [12], microphases and boundary conditions do not seem to be mentioned. Since microphases are not treated in the general macroscopic theory we now need some "model" of the interfacial zones (microphases). Such models of layers between metals and electrolytic solutions can be found in works on electrode kinetics as e.g. [6] and [8]. For the sake of simplicity we assume that all metal parts of the cell being in contact with the solution - i.e. both the wire and the wire retainers - are made of platinum allowing us to neglect any complicating exchange of metal ions between metal and solution.

The models of the interfacial layers metal - electrolytic solution have gradually been refined as they turned out to give erroneous observable consequenses. The most important investigators having been interested in this field are Helmholtz (1853 - 1879), Quincke (1861), Gouy (1910) and Chapman (1913) succeeded by Stern (1924), Grahame (1947, 1954), Macdonald and Barlow (1962) and others. Therefore one often talks about "the Helmholtz -Quincke model", "the Gouy model" and so on.

These models - which will be indicated shortly - have, as far as the author knows, not been used to explain or predict kinetic phenomena like the present one (although they are mentioned in works on electrode kinetics). They seem to have been used only - or mainly - for calculations concerning equilibrium.

In the present work such models will however be used for the estimate of the development in time of non-faradayan current pulses. This must be an obvious expansion of their ranges of applicability.

Before the models are used it should also be said that the Helmholtz- and the Gouy models were used by their originators in connection with microphysical considerations (concerning charged particles) but that the models will be "transferred" to macrophysical theory in the following. However, the author thinks that the validity of this transference may be considered as well established - for equilibrium considerations - by other more recent researchers than Gouy, e.g. Macdonald and Barlow [11].

According to the Helmholtz model of equilibrium in interfacial layers metal-electrolytic solutions,the electrons and the positive excess ions are at a cathode situated opposite each other in single "rigid" or "compact"

layers.If the model should be transferred to macrophysical theory it would correspond to singular surface layers of charge forming condensers with a distance between the charges of "atomic" order of magnitude. The Gouy model however takes into account that one cannot expect the ions (and electrons) to form such "single" layers but that - caused by thermal motion - they must be supposed to form more diffuse layers as roughly shown for a cathode (the excess ions being positive) in fig. 1. If this model is imagined transferred to macroscopical theory by "smoothig out" one obtains the following: 2 layers with continuous distributions of the components (charges) separated by a mathematical surface of discontinuity of properties. From this surface the concentrations decrease continuously and differentiably out in the macrophases. A model of this type is very suitable for macroscopic calculations of equilibrium circumstances, and it is often used in the literature for this purpose. In Forker [8] , pages 24-26 one finds e.g. a derivation of the equilibrium potential difference over the diffuse ion-layer based on it and being a special case of kinetic calculations made in the present work. Calculations of this kind in the literature are carried out for the purpose of confirming the "models" experimentally. This fact is very essential for the present work: of course one cannot introduce "models" ad hoc if one wants to predict unknown phenomena.

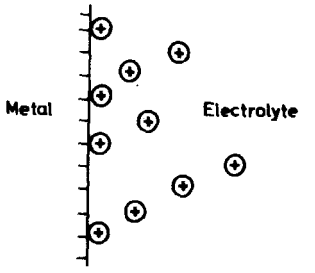


Fig.1

In other words: the word 'model' should not here be taken to mean a picture helping the imagination. Here it means a partial theory which has been incorporated into general physical theory, the whole of which has been confirmed by experiments. This is the justification of using such "models" in the present work.

In the next section we shall take the Gouy model - or strictly speaking the Gouy model transferred to macroscopical theory - as the basis. When speaking about "the Gouy model" we are thinking of the transferred one. This model, too, has its limitations and has therefore been refined by Stern and others, but the really significant step in the evolution was taken by Gouy.

It might be a little objectionable to use this very simple model, because, as a matter of fact, it gives erroneous results in many cases. But according to e.g. Macdonald and Barlow [11] the Gouy model is applicable in the limiting case of small ionic concentrations and small potential differences over the microphases. As indicated on page 18, the purpose of the present work is merely to study the lines of direction for the modification made by the author in [3] and to give a theoretical explanation of the success of that modification. The present work should by no means be taken to be an attempt to contribute originally to electrode kinetics. It is therefore deemed reasonable to confine the investigations to such idealized circumstances, where the Gouy model applies.

Outside the range of applicability of the simple Gouy model one should at least treat the problem according to Stern's modification of it. Stern modified the model by introducing a "rigid" layer of excess ions bordering directly to the metal and separating it from the diffuse Gouy layer in the liquid part of the microphase. The ions in this "rigid Helmholtz" layer may be bound by electrostatic forces or they may be "specifically adsorped". Outside the range of applicability of the simple Gouy model the "condenser" which now appears in the microphase plays a dominant role. Later and more refined models also take the polarization of the dielectric solvent into consideration. The model, which is the basis of the work [11] by Macdonald and Barlow, is the Gouy model expanded with a monolayer of dipoles of the solvent and separating the metal part from a diffuse Gouy layer in the liquid part of the microphase. These authors treat the different layers, which make up the microphase, macroscopically by their average properties. [11] is considered by the present author the best support of the considerations in the present work, in which the importance of a monolayer of dipoles will also be mentioned.

It is of course a presumption in the present work that the voltage applied to the cell is below the decomposition voltage of the electrolyte. Above this value, a "zone of reaction" must occur in which the components (electrons, ions) can meet so that chemical processes can take place and continuous electrolysis can appear. If e.g. the ions in the

diffuse "Gouy layer"*) could penetrate the surface of discontinuity of the model and also appear in the platinum part of the microphase, one would have that, at equilibrium, their chemical potentials were equal on both sides of the surface mentioned, infinetely close to it. The equilibrium condition is that the electrochemical potential of each component is constant throughout the system, and as there is no jump of the electrical potential across the surface of discontinuity of the model, there could neither be any jumps of chemical potentials. The reason why the ions keep out from the platinum parts of the microphases must be that their chemical potentials μ are so extraordinarily high in the platinum parts that, although the concentrations of the ions close to the surface of discontinuity may be rather high, they are yet too small for the μ's to reach the values in the metal part. An analogous explanation concerning the chemical potential of the electrons may be given of the fact that electrons do not appear at the liquid side of the surface of discontinuity. In other words: that the current pulse can end up with equilibrium can, according to the model, be understood through the existence of such chemical potential jumps. However, according to quantum theory, potential jumps do not prevent the penetration of "particles". From a quantum theoretical point of view the treatment given in this report is therefore, strictly speaking, inadequate. Nevertheless the calculations based on classical physics and concerning non-faradayan current pulses carried out in later sections of the present work are, in the opinion of the author, convincingly supported by corresponding investigations on equilibrium states found in treatises as e.g. [6] and [8].

c. Some Remarks on the Model with "Lumped Parameters" of the Cell Used in [3]

In connection with the above it is natural to put in a few remarks on the change from the field-theoretical treatment of the measuring cell to the use of a "model" with "lumped" electrical parameters used in the discussion in [3]

*) By 'the Gouy layer' we always understand the diffuse layer at the electrolyte side of the surface of discontinuity, not the metal part of the microphase.

During a pulse of current the instantaneous flow lines of charge in the cell must be as shown in fig. 2 which is a copy of fig. 1 in [3]. As mentioned in section I of that work the discussion of the theoretical aspects was intentionally limited there, and the change to the more handy "circuit analytic" diagram shown in fig. 3 was taken for granted.

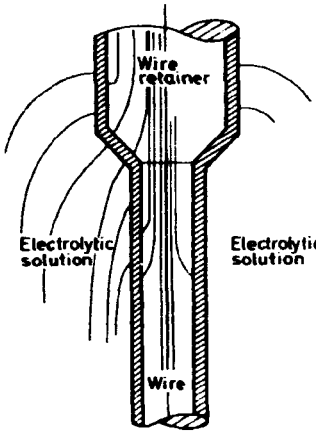


Fig. 2

Fig.3

Fig. 3 is a copy of fig. 2 in [3]. On page 15 of the last-mentioned work it was said that the change fig. 2 → fig. 3 is "evident". A closer inspection shows, however, that this evidence should be taken with a grain of salt but we shall later see that fig. 3 must be considered fully adequate for the purpose in [3]. However, we shall not interrupt the exposition by discussing the "geometry of the fields" in this place. After all, such a discussion is of minor importance in the present context and we therefore postpone it. But there is another question that deserves a few remarks here. In fig. 3 the microphases are represented by electromotive forces $\mathcal{E}_1$ and $\mathcal{E}_2$. In so far as it is at all permissible to change from field theoretical description to descriptions with lumped parameters in the present context, the representation referred to is justified by the Gouy model (cf. equation (12)). But in connection with fig. 3 the following equations were put forward ([3], page 15).

$$\left.\begin{aligned} \Delta\varphi_c &= R_L J_L + \mathcal{E} \\ \Delta\varphi_c &= R_W J_W \\ \mathcal{E} &= \mathcal{E}_1 + \mathcal{E}_2 \end{aligned}\right\} \qquad (18)$$

where

$\Delta\varphi_c$ = voltage applied to the cell

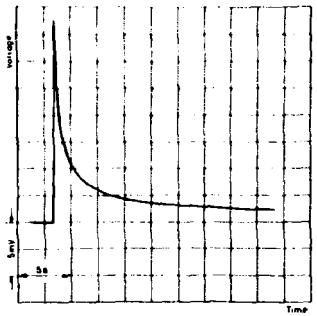
R_L = resistance of the solution column

J_L = current in the solution

R_W = resistance of the wire

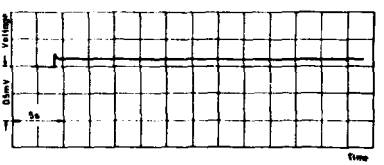
J_W = current in the wire

(18) constituted the basis of the discussion of the experiments in [3] . Now (18) is built upon Ohm's law without the term accounting for induction. As it is strongly emphasized in the small print text, page 20 , that one cannot leave out the term ' $-\sigma \frac{\partial \vec{A}}{\partial t}$ ' in e.g. (12), the analysis may seem to be erroneous. But (18) is based on Ohm's law on integrated form i.e. integrated over the lengths of 2 paths in the cell and the corresponding cross sections, and although it will be absolutely erroneous to leave out ' $-\sigma \frac{\partial \vec{A}}{\partial t}$ ' in (12), it may be quite in order to neglect the integral of this term compared with the other integral terms. From an integral over a fixed region being 0 or negligible, one cannot infer that the integrand is also 0 or negligible at every point of the region. A certain hint that one can treat the current pulses without regard to induction in the integrated equations is given by figs. 4 and 5, which are copies of figs. 11 and 12 in [3] . Incidentally these figures can be said roughly to illustrate the essence of the modification (note the differnt scales on the voltage axes of the 2 figures). They show the course of development of the recorded voltage - with positive direction downwards - during "blank experiments" where - as mentioned in section I - the platinum wire has been replaced by a manganin wire in an unmodified set-up (fig. 4) and in a modified one (fig. 5). At such experiments no registrations of the heating of the wire occur. The only thing recorded is the voltage alterations during current pulses. Now, the registered pulses may very well be "faradayan", but as mentioned above all pulses must be "non-faradayan" at the outset. If induction played a role one might expect the curves at least to



Blank experiment in "classical" set-up on 0.5 N NaCl
I = 0.21 A

Fig.4



Blank experiment in modified set-up on about 2N Na OH
I = 3.8 A

Fig.5

begin as wavy lines. True, the waves might in principle have died out so fast that the recorder could not register them. But then they would have died out so quickly that it seems reasonable to ignore them in our context. As a matter of fact in all the following calculations on non-faradayan pulses the terms due to induction in the integrated forms of Ohm's law will be ignored.

There is also another objection to the analysis in [3] that might be set forth. The analysis is built upon neglecting the terms of the form $\frac{\varepsilon}{\sigma}\frac{dJ}{dt}$ (ε = dielectric permeability) - i.e. the terms due to "displacement currents" - in the boundary conditions (cf page 14 in [3]). During the very quick initial part of the pulses this assumption is not valid, but the blank experiments - as treated in [3] on the basis of the assumption - are mainly thought to account for the later, slower development in the cell. Now the small peak in the diagram fig. 5 is easily seen from the analysis in [3] to be only "a rudiment" of a much larger peak, which could not be registered by the recorder owing to its inertia. But it is also seen from fig. 5 that the larger

part of the peak would be recorded only as a segment in the direction of the voltage axis if the recorder had no inertia. In other words, the process represented by the unregistered part of the peak is over "instantaneously" in the modified apparatus. Therefore the analysis in [3] can be considered valid instantaneously for this apparatus although the "displacement currents" are ignored. This point will be treated in more detail later on.

III. Investigation of the Simplest Case of Current Pulses Below the Decomposition Voltage in an Electrolysis System

We shall now turn to the investigation of the development in time of non-faradayan pulses, and in this section we shall confine ourselves to the study of the simplest case. We will so to speak study the "pure phenomenon" by letting out of consideration such complicating circumstances as the external resistance in the leads to the cell and the geometrical problems owing to the wire and the wire retainers. In other words the wire is imagined removed and the electrodes formed as platinum discs, constituting the bottom and the top of the cylindrical cell. Furthermore this "measuring cell" is thought to be connected directly to a source cell with a (constant) terminal voltage P less than the decomposition voltage of the electrolytic solution in the "measuring cell".

If the Helmholtz model could be applied one would have a very simple problem, namely that corresponding to the diagram fig. 6 showing 2 condensers in series with the resistance ρ_L of the liquid column. This

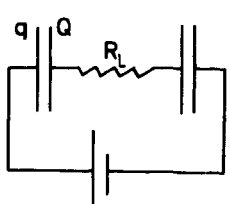


Fig.6

"model" will be considered a little closer, because - although being very trivial and quite elementary it gives occasion for some remarks which are relevant later on. The plates of the condensers are imagined made of metal. Let us consider e.g. the left condenser and let q and Q be the charges on its plates. (See the figure) According to the preceding section q and Q should strictly speaking form diffuse layers, but in metal plates we may consider the charges as being surface distributed, the interior of the metal being neutral (seen from a macroscopical point of view). Owing to the order of magnitude of the charge or. mole, it must be stoichiometrically quite vanishing small amounts of electrons which participate in the charging of the condensers, so that no concentration differences of electrons can contribute to differences in their chemical potential in the plates. The chemical potential of the electron may therefore - at constant temperature - be considerd nearly constant in the metal, and we see that no electromotive forces owing to "diffuse" distributions appear. (cf. (12) applied to electrons). If the charges were made up of amounts of electrons which could e.g. be directly weighed, the voltage over the condensers would be unimaginably high*). Let us now ignore the dielectric polarization phenomena i.e. put the dielectric permeability $\varepsilon = \varepsilon_0$ = ε's value in vacuum through the whole system. According to the surface distribution of the charges, the electric field $\vec{E}$ will show a jump when passing e.g. the charge q of the left condenser in the right-hand direction. The jump in $|\vec{E}|$ has the magnitude $\frac{q}{\varepsilon a}$, 'a' denoting the area of the plate. Just before the passage one has $\vec{E} = \frac{\vec{i}_1}{\sigma}$, where σ = specific conductivity of the metal and $\vec{i}_1$ = the current density. As there are no charges in the space between the plates, $\vec{E}$ is only dependent upon t there, and directed in the normal direction z of the condenser (The plates are assumed to be very large perpendicular to z). So in the space mentioned one has according to (2)

$$-\frac{\partial \varphi}{\partial z} - \frac{\partial A_z}{\partial t} = \frac{i_1}{\sigma} + \frac{q}{\varepsilon_0 a} \quad ,$$

where A_z = the z component of $\vec{A}$ and $i_1 = |\vec{i}_1|$ taken with the right sign. Hence, integrating over the distance l_1 between the plates, one has

---

*) Let e.g. q (or Q) = the charge of 1 mole of electrons, i.e. $\frac{1}{1850}$ g, and let

$\Delta\varphi$ = the voltage difference over the left condenser, measured in volt.

$\varepsilon = \varepsilon_{water} \sim 7 \cdot 10^{-10}$ farad m^{-1} = the dielectric permeability of the material that fills the gap between q and Q

l = the distance between q and Q, measured in m.

a = the area of the plates, measured in m^2

one then finds

$$\Delta\varphi = q \frac{l}{\varepsilon a} = 96500 \cdot 10^{10} \cdot \frac{l}{7} \cdot \frac{1}{a}$$

and it is seen that, although l may, as mentioned shortly, be of "atomic" order of magnitude, $\Delta\varphi$ will be extraordinarily high if the plates are not quite extremely large.

$$-\Delta_1\varphi = \frac{q}{\varepsilon_0 s} l_1 + \frac{\overline{\partial A}}{\partial t} l_1 + i_1 r_1$$

where the bar indicates the mean value and r_1 = the resistance of a piece of metal of length l_1 and unity area. Now, l_1 must be extremely small. Parker [8] gives page 20 for interfacial layers metal-electrolytic solution in equilibrium "thicknesses" of 10^{-8} - 10^{-6} cm. So if the condensers should really represent the microphases, l_1 can be said to be so small that with very good approximation one may put

$$-\Delta\varphi_1 = \frac{q}{\varepsilon_0 s} l_1 + l_1 \frac{\overline{\partial A_z}}{\partial t} \quad ;$$

or

$$-\Delta\varphi_1 = \frac{q}{C_1} + L_1 \ ,$$

where

$$C_1 = \frac{\varepsilon_0 s}{l_1} = \text{the capacity of the left condenser}$$

and

$$L_1 = l_1 \frac{\overline{\partial A_z}}{\partial t} \quad (\simeq 0 \text{ if } \frac{\overline{\partial A_z}}{\partial t} \text{ is not extremely high})$$

Analogous reasoning concerning the right-hand side plate gives the corresponding expression for $\Delta_1\varphi$ expressed by Q instead of by q, and one therefore finds with very good approximation, that during the charging

$$Q + q = 0 \tag{19}$$

Analogous reasoning concerning the right-hand side condenser with capacity C_2 gives its $\Delta\varphi$, $\Delta_2\varphi$, and a circuit analysis (during which the current J_L in R_L is put numerically equal to $\frac{dq}{dt}$) can be made:

$$P = |\Delta_1\varphi| + |\Delta_2\varphi| + R_L J_L + L$$

Here P is, as before, the terminal voltage of the source cell and 'L' is "the integrated" term due to induction. In accordance with what is said on page 27, 'L' is left out and we find, if P = const and this equation is differentiated with respect to time, the well known equation

$$\dot{q}\left(\frac{1}{C_1}+\frac{1}{C_2}\right)+R_L\ddot{q}=0 \qquad (20)$$

which is solved by

$$\left.\begin{aligned} q &= q_0\left(1-e^{-\frac{t}{R_L C}}\right) \\ J &= J_0\, e^{-\frac{t}{R_L C}} \end{aligned}\right\} \qquad (20a)$$

Here subscript '0' indicates initial values.

Furthermore

$$\frac{1}{C}=\frac{1}{C_1}+\frac{1}{C_2} \qquad (20b)$$

If the Helmholtz model were applicable we would, as shown in the text written in small print, and as is well known have

$$J_L = J_o\, e^{-\frac{t}{R_L C}},$$

(cf (20a) and (20b). But C would not be known. C is the capacity of the 2 condensers in series, and for the calculation of it we need the distances of the charges. According to a remark in the small print text one might estimate these distances to lie in the interval 10^{-4} - 10^{-8} cm.

If one accepts the mentioned interval as being the interval of the distances between the charges one finds with e.g. $R_L \simeq 5\ \Omega$, $C_1 \simeq C_2$ and plate area $\simeq 3 \cdot 10^{-3}\ m^2$ for the relaxation time (time constant) $\tau = R_L C$, using the value $\varepsilon_o \simeq 10^{-11}$ farad m^{-1}

$$7 \cdot 10^{-8}\ s < \tau < 7 \cdot 10^{-4}\ s.$$

Quite apart from this interval of indeterminedness being very large, it is known from the previous discussion, that the Helmholtz model is nowadays not considered reliable (even not for quantitative treatment of equilibrium problems). We shall therefore carry through the calculations using the Gouy model.

What can be taken over from the elementary reasoning in the small print text, where the Helmholtz model is used, is only that one may consider the diffuse layers in the metal parts of the microphases as degenerating to surface distributed charges *) and therefore the electromotive forces in these parts as negligible. Thus the whole difference in voltage across the microphases (needed in the circuit analysis) can be considered to occur across the diffuse "Gouy layers" in the electrolytic parts of the microphases, when using the Gouy model. The problem therefore mainly consists in finding such potential differences. To do this without unnecessary complications one may also take over, at least at the outset, the presumption that the dielectric permeability $\varepsilon = \varepsilon_0$ = its value in vacuum through the whole system. So the variation of ε through the diffuse layers is ignored, and we shall totally ignore dielectric polarization phenomena. Furthermore it simplifies matters essentially if also the variation of σ through the diffuse Gouy layers is ignored.

Under these presumptions it is easy to derive **) from (1), (2) and (3) - as valid in these layers - the equations

$$\nabla^2\varphi - \mu_0\varepsilon_0\ddot{\varphi} + \frac{\partial}{\partial t}\left(\operatorname{div}\vec{A} + \mu_0\varepsilon_0\dot{\varphi}\right) = -\frac{\rho}{\varepsilon_0} \qquad (21)$$

$$\nabla^2\vec{A} - \mu_0\varepsilon_0\ddot{\vec{A}} - \operatorname{grad}\left(\operatorname{div}\vec{A} + \mu_0\varepsilon_0\dot{\varphi}\right) = -\mu_0\vec{i}\ , \qquad (21a)$$

where dots indicate derivatives with respect to time, and 'ρ' and '$\vec{i}$' mean the densities of charge and current respectively. If a guage in which $\operatorname{div}\vec{A} = 0$ is chosen, one thus finds from (21) an equation of the simple "Poisson form"

$$\nabla^2\varphi = -\frac{\rho}{\varepsilon_0}\ , \qquad (22)$$

but φ and ρ shall here be taken as functions of time as well as of the space coordinates. For space coordinates we shall, on account of the rotational symmetry round the cell axis, which may be presumed for the fields, use a polar system with the said axis as z axis and r as radial coordinate. (22) can then be written

$$\frac{\partial^2\varphi}{\partial z^2} + \frac{1}{r}\frac{\partial\left(r\frac{\partial\varphi}{\partial r}\right)}{\partial r} = -\frac{\rho}{\varepsilon_0}\ , \qquad (23)$$

where $\varphi = \varphi(r,z,t)$ and $\rho = \rho(r,z,t)$

*) The reason why the ions in the Gouy layer can on the other hand be diffusely distributed is given in a footnote on page 36.

**) see e.g. Born [4], page 72. (Born does not use the modern system of units used here). μ_0 is μ's value for vacuum.

The equation for $\vec{A}$ in the said gauge reads

$$\nabla^2\vec{A} - \mu_o\varepsilon_o\ddot{\vec{A}} = -\mu_o\vec{i} + \mu_o\varepsilon_o \operatorname{grad}\dot{\varphi} \quad .$$

The gauge $\operatorname{div}\vec{A} = 0$ is a little unusual (it is e.g. not Lorentz invariant). The "usual" gauge is one, in which $\operatorname{div}\vec{A} + \mu_o\varepsilon_o\dot{\varphi} = 0$. In that gauge (21) and (21a) give wave equations for both φ and $\vec{A}$. But it will be reasonable to consider the alterations of the fields - although being fast at the very initial stages - sufficiently slow for ignoring the "retardations" owing to the "wave terms", $\mu_o\varepsilon_o\ddot{\varphi}$ and $\mu_o\varepsilon_o\ddot{\vec{A}}$, and to use (22) for φ without further discussion of choice of gauge.

It would be an essential simplification to be able to treat the whole problem as one-dimensional so that (22) could be written

$$\frac{\partial^2\varphi}{\partial z^2} = -\frac{\rho}{\varepsilon_o} \quad , \tag{24}$$

but in the curved microphase between the cell wall and the solution there must be radial concentration gradients of the ions. Thus there are radial electromotive forces in these layers which must at the later stages be balanced by radial components of $\operatorname{grad}\varphi$ (cf. (12)). Thus, at any rate when the liquid part of the said curved layer is included in the region under considerations as is the case later on, (24) is not valid througout the whole region.

However, let A_c be the cross section area of the cell, and let us integrate (23) over a cell cross section situated in a Gouy layer between an electrode plate and the electrolytic solution. Denoting the mean value $\frac{1}{A_c}\int\varphi\,dA_c$ by '$\bar{\varphi}$' and the radius of the cell by 'r_c', one finds

$$\frac{\partial^2\bar{\varphi}}{\partial z^2} + \frac{2}{r_c}\left(\frac{\partial\varphi}{\partial r}\right)_{r=r_c} = -\frac{\bar{\rho}}{\varepsilon_o} \quad , \tag{25}$$

where $\bar{\rho}$ is the mean value of ρ over the section. What is needed in the following is mainly the result of integrating (25) through the Gouy layer. Let 'M' indicate the boundary surface between metal and Gouy layer and let 'O' indicate the boundary surface between Gouy layer and solution. By integration through the layer is found

$$\left(\frac{\partial\bar{\varphi}}{\partial z}\right)_O - \left(\frac{\partial\bar{\varphi}}{\partial z}\right)_M + \frac{2}{r_c} l \left(\frac{\partial\tilde{\varphi}}{\partial r}\right)_{r=r_c} = -\int_M^O \frac{\bar{\rho}}{\varepsilon_o}\, dz \quad , \tag{26}$$

where the tilde indicates the mean value when integrating through the layer in the z direction, and l is the thickness of the layer. In the following partial derivatives are indicated by a subscript, giving the coordinate with respect to which we differentiate. Furthermore the following definition is used

$$\bar{q} = \int_M^O \bar{\rho}\, dz \tag{27}$$

and (26) can now be written

$$(\bar{\varphi}_z)_O - (\bar{\varphi}_z)_M + \frac{2}{r_c} l (\tilde{\varphi}_r)_{r=r_c} = -\frac{\bar{q}}{\varepsilon_o} .$$

$(\tilde{\varphi}_r)_{r=r_c}$ may be assumed to be of the same order of magnitude as $(\varphi_z)_M$ or presumably less, owing to the geometrical shape of the system and to the applied voltage being directed in the z direction. Furthermore the factor $\frac{2}{r_c} l$ is according to the inequality $10^{-8}\text{cm} < l < 10^{-4}\text{cm}$ very small. It must therefore be reasonable to put

$$(\bar{\varphi}_z)_O - (\bar{\varphi}_z)_M = -\frac{\bar{q}}{\varepsilon_o} \tag{28}$$

It is not quite correct to say that what is needed in the following is only the mentioned integration through the microphases. Later on it is necessary also to derive an expression where $(\bar{\varphi}_z)^2$ and $(\bar{\varphi}_z)^2$ appear. Also in that expression we leave out a term in which $(\varphi_r)_{r=r_c}$ appears during an integration. An integral of the type

$$\int \frac{2}{r_c} (\varphi_r)_{r=r_c} \bar{\varphi}_z\, dz$$

plays a role in that derivation, but it can also be evaluated according to the mean value theorem. One will then find by analogous reasoning to the above that also by this application of (25) the term originating in φ-variation in the r direction may be neglected.

For the sake of simplicity we consider only an electrolyte completely dissociated in one positive ion, the mole fraction of which is denoted by 'x_+', and one negative ion with molefraction x_-. The chemical potentials and the mass flow densities of these ions are μ_+ and μ_- and $\vec{j}_+$ and $\vec{j}_-$ respectively. In the diffuse Gouy layer one has, according*) to (15),

$$\text{grad } \mu_+ - F\vec{E} = B^*_{11}\vec{j}_+ + B^*_{12}\vec{j}_- , \tag{29}$$

and an analogous expression for μ_-. If the mass flow density of H_2O in the diffuse layers is ignored as compared to $\vec{j}_+$ and $\vec{j}_-$, it is seen that the right hand side of (29) can be written on the form $\frac{\vec{i}}{\sigma_+}F$ because, as mentioned in section II, the sum of all diffusion mass flow densities is $\vec{0}$ ($\vec{i}$ is the total electrical flow density). Hence

$$-\text{grad } \mu_+ + F\vec{E} = \frac{\vec{i}}{\sigma_+}F$$

The order of magnitude of σ_+ and σ must be the same, i.e.

$$-\frac{\partial \mu_+}{\partial z} + F E_z \simeq \frac{i_z}{\sigma} F \tag{30}$$

where subscript 'z' means the z component of a vector. Forming mean values over the cross section mentioned above, we have from (30)

$$-\frac{\partial \bar{\mu}_+}{\partial z} + F \bar{E}_z \simeq \frac{\bar{i}_z}{\sigma} F, \tag{31}$$

where the barred symbols designate values taken at a certain $r = r^*$ (at a given time t) and where $0 < r^* < r_c$. Using (2), (14) and (31) for $r = r^*$, $T \simeq$ const. and integrating through a Gouy layer one has

$$RT \ln \frac{(\bar{x}_+)_M}{(\bar{x}_+)_O} + F(\bar{\varphi}_M - \bar{\varphi}_O) \simeq F R_G J_z + L_z F, \tag{32}$$

The meaning of the barred symbols in (32) is immediatly clear. R_G is the resistance of the layer in the z direction, and J_z is the total current in this direction taken at a suitable z in the layer. $L_z F$ is the contribution to the result from $\frac{\partial \Delta z}{\partial t}$. If one introduces '$\bar{\delta}$' defined by

*) The ions are assumed to be monovalent.

$$\bar{\delta} = \bar{\varphi}_O - \bar{\varphi}_M \quad , \tag{33}$$

one then has

$$\bar{\delta} + R_G J_z + L_z = \frac{RT}{F} \ln \frac{(\bar{x}_+)_M}{(\bar{x}_+)_O} \quad , \tag{34}$$

The mole fraction of the ions in the macrophase of the solution will now be put = x. For the sake of convenience subscript 'M' is also dropped so that x_+ is now the value of x_+ at the surface, where the Gouy layer borders to the metal. Thus from (34) is found

$$\bar{\delta} + R_G J_z + L_z = \frac{RT}{F} \ln \frac{\bar{x}_+}{x} \quad , \text{ with } \begin{cases} x = (\bar{x}_+)_O \\ \bar{x}_+ = (\bar{x}_+)_M \end{cases} . \tag{34a}$$

For the charge density ρ in the layer one has, 'F' as usually designating 96500 coulomb $mole^{-1}$,

$$\rho = F\,(c_+ - c_-), \tag{35}$$

where the c's are the molarities of the positive and negative ions respectively.*) But under our presumptions (diluted solutions) we have

$$\frac{\bar{x}_+}{x} \simeq \frac{\bar{c}_+}{c} \quad ,$$

c being the molarity corresponding to x, so that according to (34a)

$$\frac{(\bar{c}_+)_M}{c} = e^{\frac{F}{RT}\,(\bar{\delta} + R_G J_z + L_z)} \quad , \tag{36}$$

(36) shall now be used to find the factor $\bar{\delta} + R_G J_z + L_z$ in the exponent in order to use it in a circuit analysis. In such an analysis $R_G J_z$ will be quite negligible as compared to other terms of the form "current multiplied by resistance", and L_z adds up with other contributions from induction. As remarked on page 27 we shall neglect induction in the integrated equations, and we may therefore continue as if we had

---

*) In the metal, we argued on page 29, the gradient of the electron concentration is $\simeq 0$. (35) only requires that $\mathrm{grad}(c_+ - c_-) \simeq 0$ which does not prevent $|\mathrm{grad}\, c_+|$ and $|\mathrm{grad}\, c_-|$ from being high. That is the reason why the ions can form diffuse layers, but the electrons cannot.

$$\frac{(\bar{c}_+)_M}{c} = \frac{\bar{c}_+}{c} = e^{\frac{F}{RT}\bar{\delta}} \quad , \tag{37}$$

The meaning of '$(c_+)_M$' = 'c_+' will now be changed: (37) holds equally good if 'c_+' means c_+ at an arbitrary z-value in the Gouy layer and if the meaning of $\bar{\delta}$ is correspondingly changed. Furthermore we note that an expression anologous to (37) can, by the corresponding procedure, be derived for c_-. The "Poisson equation" (24) (with barred symbols), together with (36), then gives

$$\frac{\partial^2 \bar{\varphi}}{\partial z^2} = -\frac{F}{\varepsilon_o}(\bar{c}_+ - \bar{c}_-) = \alpha \left\{ e^{\beta(\bar{\varphi} - \bar{\varphi}_o)} - e^{-\beta(\bar{\varphi} - \bar{\varphi}_o)} \right\} \quad , \tag{38}$$

where

$$\alpha = \frac{F}{\varepsilon_o} c$$

$$\beta = \frac{F}{RT} \quad ,$$

$\bar{\varphi}$ = the $\bar{\varphi}$-value at an arbitrary z in the Gouy layer.

$\bar{\varphi}_o$ = the $\bar{\varphi}$-value at the boundary between the Gouy layer and the bulk of the solution.

(38) may be written

$$\frac{\partial^2 \bar{\varphi}}{\partial z^2} = 2\alpha \sinh(\beta(\bar{\varphi} - \bar{\varphi}_o)) \quad ,$$

or

$$\bar{\varphi}_{zz} = 2\alpha \sinh(\beta(\bar{\varphi} - \bar{\varphi}_o)) \quad ,$$

Multiplying this equation by $\bar{\varphi}_z = \frac{\partial \bar{\varphi}}{\partial z}$ and integrating across the layer one finds

$$(\bar{\varphi}_z)_O^2 - (\bar{\varphi}_z)_M^2 = 4\alpha \int_M^O \sinh(\beta(\bar{\varphi} - \bar{\varphi}_o))\, d\bar{\varphi} \quad ,$$

which, when the integration is carried out, and (33) is used gives

$$(\bar{\varphi}_z)_O^2 - (\bar{\varphi}_z)_M^2 = \frac{4\alpha}{\beta}(1 - \cosh(\beta\bar{\delta})) \quad , \tag{39}$$

Here use has been made of (24) with barred symbols instead of (25). This is justified by the remarks in the small print text of pages 34-35. From the definition (27) of $\bar{q}$ and from (28) and (39) we get

$$\sqrt{2}\sinh\frac{\beta\bar{\delta}}{2} = \pm\sqrt{\frac{\beta}{4\alpha}}\sqrt{\left(\frac{\bar{q}^2}{\varepsilon_o^2} + 2\frac{\bar{q}\,(\bar{\varphi}_z)_O}{\varepsilon_o}\right)}$$

i.e.

$$\pm\frac{\beta\bar{\delta}}{2} = \ln\sqrt{\frac{\beta}{8\alpha}} + \ln\left\{\sqrt{\left(\frac{\bar{q}^2}{\varepsilon_o^2} + \frac{2\,\bar{q}\,(\bar{\varphi}_z)_O}{\varepsilon_o}\right)} + \sqrt{\left(\frac{\bar{q}^2}{\varepsilon_o^2} + \frac{2\,\bar{q}\,(\bar{\varphi}_z)_O}{\varepsilon_o} + \frac{8\alpha}{\beta}\right)}\right\} \quad (40)$$

As '$(\bar{\varphi}_z)_o$' means $\bar{\varphi}_z$ at the boundary between the microphase and the electrolytic macrophase where $\vec{\mathcal{E}}$ in (12) is = $\vec{0}$, we have at equilibrium $(\bar{\varphi}_z)_o = 0$, and (40) reduces to

$$\pm\bar{\delta} = \frac{2}{\beta}\left\{\ln\sqrt{\frac{\beta}{8\alpha}} + \ln\left\{\frac{|\bar{q}|}{\varepsilon_o} + \sqrt{\left(\frac{\bar{q}^2}{\varepsilon_o^2} + \frac{8\alpha}{\beta}\right)}\right\}\right\} \quad (41)$$

which when using the definitions of α and β in (38) will be found to agree with what Forker [6] gives on page 26 for equilibrium in a one-dimensional layer (without bars over the symbols).

The above integration was performed through the diffuse Gouy layer, i.e. not including the surface distributed layer in the metal. One might as well integrate across the whole microphase, including the surface charge (per unit area) in the metal. This gives

$$(\bar{\varphi}_z)_O - (\bar{\varphi}_z)_P = -\frac{\Delta\bar{q}}{\varepsilon_o}, \quad (42)$$

where index 'P' indicates value in the metal electrode infinitely close to the surface charge, and Δq is the total charge pr. unit area of the whole microphase. In the "condenser problem" treated in small print page 30 (19) was derived and dividing by the cross section area of the plates, one would have $\Delta\bar{q} = 0$ if one could derive an equation like (19) in the present case. This is not possible, but if we confine ourselves to small applied voltages, $|\Delta\bar{q}|$ will always be small as compared to $|\bar{q}|$. Owing to the very high value of σ in the metal, $(\varphi_z)_P$ must also be expected to be rather small during nearly the whole of the passing off of the pulse. It is therefore reasonable to put

$$(\varphi_z)_O \simeq -\frac{\Delta\bar{q}}{\varepsilon_o}$$

instead of using (42) and to neglect the term $2\frac{\bar{q}\,(\bar{v}_z)'_o}{\varepsilon_o}$ under the square root sign in (40). This equation then reduces to the "equilibrium expression" (41):

$$\pm\bar{\delta} = \frac{2}{\beta}\left\{\ln\sqrt{\frac{\beta}{8\alpha}} + \ln\left\{\frac{|\bar{q}|}{\varepsilon_o} + \sqrt{\left(\frac{\bar{q}^2}{\varepsilon_o^2} + \frac{8\alpha}{\beta}\right)}\right\}\right\} .$$

If one differentiates (41) with respect to $|\bar{q}|$ at constant c (c is a factor in the expression for α), one finds

$$\frac{d|\bar{\delta}|}{d|\bar{q}|} = \frac{2}{\beta\varepsilon_o}\,\frac{1}{\sqrt{\left(\frac{\bar{q}^2}{\varepsilon_o^2} + \frac{8\alpha}{\beta}\right)}} . \qquad (43)$$

During the whole investigation in this section we have - merely for reasons of convenience - written 'ε_o' throughout in our formulae neglecting dielectric polarization totally. But if we use the (constant) value ε_w = the dielectric permeability of water in the Gouy layers the approximation will presumably be improved. Instead of (43)

$$\frac{d|\bar{\delta}|}{d|\bar{q}|} = \frac{2}{\beta\varepsilon_w}\,\frac{1}{\sqrt{\left(\frac{\bar{q}^2}{\varepsilon_w^2} + \frac{8\alpha}{\beta}\right)}} , \quad \text{with } \alpha = \frac{F}{\varepsilon_w}c \qquad (44)$$

is therefore used. From (44) follows - a dot meaning as usual derivative with respect to time -

$$|\dot{\bar{\delta}}| = \frac{2}{\beta\varepsilon_w}\,\frac{|\dot{\bar{q}}|}{\sqrt{\left(\frac{\bar{q}^2}{\varepsilon_w^2} + \frac{8\alpha}{\beta}\right)}} . \qquad (45)$$

(45) will now be combined with a circuit analysis analogous to what was done in the small print text, page 30 , where the Helmholtz model was used. In the electrolytic macrophase - where there are no x-gradients during the pulse of current - one has, according to (12) (with $\vec{\mathcal{E}} = \vec{0}$),

$$\frac{i_z}{\sigma} = -\frac{\partial\varphi}{\partial z} - \frac{\partial A_z}{\partial t} .$$

Integrating over the cell cross section with area A_c, one finds

$$\frac{i}{\sigma}\int_{A_c} i_z\, dA_c = -\frac{\partial\bar{\varphi}}{\partial z} A_c - \bar{I},$$

$\bar{I}$ being $= -\int_{A_c} \frac{\partial Az}{\partial t}\, dA_c$. Now $\int_{A_c} i_z\, dA_c$ is the current through an arbitrary cross section in the z direction J_z, and one finds

$$\frac{1}{\sigma A_c} J_z = -\frac{\partial\bar{\varphi}}{\partial z} - \frac{\bar{I}}{A_c} \quad .$$

If the charge transport in the z direction through the liquid part of the curved microphase between cell wall and solution is included J_z must be constant, i.e. independent of z (but not of t, of course). If the length of the cell is h, one therefore finds for the potential difference $\Delta\bar{\varphi}_m$ over the macrophase in the cell

$$\Delta\bar{\varphi}_m = \frac{h}{\sigma A_c} J_z + L' = R_L J_z + L' \quad ,$$

where L' is the contribution from induction which, as mentioned in the above, will be neglected in the final circuit analysis so that one can write

$$\Delta\bar{\varphi}_m = R_L J_z = R_L \cdot A_c \cdot \dot{\bar{q}} = \frac{h}{\sigma}\dot{\bar{q}} \quad . \tag{46}$$

If the "jumps" $|\bar{\delta}_1|$ and $|\bar{\delta}_2|$ in the layers at the electrode plates are added to $\Delta\bar{\varphi}_m$ (cf. (33)) the result of the circuit analysis will read

$$P = \text{terminal voltage} = \Delta\bar{\varphi}_m + |\bar{\delta}_1| + |\bar{\delta}_2|$$

because the resistance in the leads to the simplified "measuring cell" is neglected. Considering P as constant one has

$$0 = \dot{\Delta\varphi}_m + |\dot{\bar{\delta}}_1| + |\dot{\bar{\delta}}_2| \quad ,$$

By aid of (45) and (46) one therefore ends up with the following differential equation for the current pulse:

$$\frac{4\,\dot{\bar{q}}}{\beta\sqrt{\bar{q}^2 + \frac{8\alpha}{\beta}\,\epsilon_w^2}} + \frac{h}{\sigma}\ddot{\bar{q}} = 0 \quad . \tag{47}$$

If one compares (47) with the equation (20) obtained by using the Helmholtz model it is seen that, at least in principle, the problem is more complicated than it would be according to the simple Helmholtz model. (47) is, as opposed to (20), not linear and therefore more difficult to solve. Hence we do not carry through the solution of it which would - under the simplifying assumptions made - be the solution of the problem of this section. One can, however, very easily determine the passing off of the pulses within limits sufficient for the present purpose using (47) and some estimations.

Incidentally it is very easy to find a first integral to (47). If (47) is written on the form

$$\frac{\dot{\bar{q}}}{\sqrt{(\bar{q}^2 + n)}} + a\ddot{\bar{q}} = 0 ,$$

with n = const, a = const, one finds by putting $\dot{\bar{q}} = p$, i.e. $\ddot{\bar{q}} = p\frac{dp}{d\bar{q}}$:

$$\frac{1}{\sqrt{(\bar{q}^2 + n)}} + a\frac{dp}{d\bar{q}} = 0 ,$$

i.e.

$$a\,p = -\int \frac{d\bar{q}}{\sqrt{(\bar{q}^2 + n)}} ,$$

Thus

$$\dot{\bar{q}} = -\frac{1}{a} \ln \left| \bar{q} + \sqrt{(\bar{q}^2 + n)} \right| + \text{const}$$

is a first integral. Using this first integral, one finds the solution in the form

$$t = -a\int \frac{d\bar{q}}{\ln\left|\bar{q} + \sqrt{(\bar{q}^2 + n)}\right| + \text{const}} + \text{const}',$$

but this is not a handy expression and, as said, the exact solution will not be discussed in further details.

The non-linearity of (47) stems from (44) which shows that we do not - as for a simple condenser - have proportionality between voltage difference and charge in the microphases. Thus we cannot, independent of the charge

talk about a capacity but only about "a differential capacity", which (per unit area) is given as $\frac{d\bar{q}}{d|\bar{\delta}|}$ by taking the reciprocal of equation (44). Now Forker [8] gives page 22 that as results of experiments this quantity (for equilibrium) has values between 5 and 50 μfarad cm^{-2} - i.e. between 0,05 and 0,5 farad m^{-2} - for layers between metal electrodes and aqueous electrolytic solutions. We therefore have, Φ being the function $\frac{2}{\beta\, \epsilon_w \sqrt{(\frac{\bar{q}^2}{\epsilon_w^2} + \frac{8\alpha}{\beta})}}$, from (47):

$$\left.\begin{aligned} &2 \Phi(\bar{q})\, \dot{\bar{q}} + \frac{h}{\sigma}\, \ddot{\bar{q}} = 0 \\ &2 < \Phi(q) < 20 \end{aligned}\right\} \qquad (48)$$

which may be used for an estimate of the passing off of the pulse.

It cannot be objected that one might have written down (48) immediately so that the whole discussion above is superfluous. The values 2 and 20 are as said equilibrium values for the reciprocal of the differential capacity per unit area, but this quantity might have turned out to be e.g. strongly dependent also on $\dot{\bar{q}}$. The approximation made by using the "equilibrium expression" (48) (cf (40), where $\bar{\varphi}_2{}'_0$ appears) first had to be justified.

Now, as $\bar{q}$ satisfies a second order differential equation, one has $\bar{q} = \bar{q}\,(t, c_1, c_2)$ where c_1 and c_2 are integration constants. If this is substituted into Φ we find, say, $\Phi(\bar{q}) = \psi\,(t, c_1, c_2)$, and, according to (48)

$$\left.\begin{aligned} &2 \psi\ (t, c_1, c_2)\, \dot{\bar{q}} + \frac{h}{\sigma}\, \ddot{\bar{q}} = 0 \\ &2 < \psi < 20 \end{aligned}\right\} \qquad (49)$$

or, if one multiplies by the cross section area,

$$\left.\begin{aligned} &2 \psi\ J_L + \frac{h}{\sigma}\, \dot{J}_L = 0 \\ &2 < \psi < 20 \end{aligned}\right\} \qquad (50)$$

where J_L is, as usual, the current in the liquid. Integrating, one finds

$$J_L = J_L^o\, e^{-\int_o^t \frac{2\psi}{h}\, \sigma\, dt}$$

J_L^o being J_L's initial value. Hence using the inequalities in (49):

$$J_L^o e^{-40\frac{\sigma}{h}t} < J_L < J_L^o e^{-4\frac{\sigma}{h}t}$$

In other words: J_L's development in time is in the most favourable case almost an exponential decrease with time constant

$$\tau_1 = \frac{h}{40\sigma}$$

and in the most unfavourable case almost an exponential decrease with time constant

$$\tau_2 = \frac{h}{4\sigma}$$

We may rewrite '$\frac{h}{\sigma}$' as '$A_c R_L$' (A_c = cross section of the cell, R_L = resistance of the liquid column) for easier comparison with the result obtained by using the Helmholtz model on page 31 . Using $A_c = 3 \cdot 10^{-3}$ m^2 and $R_L = 5\,\Omega$ as we did there, we have

$$\left.\begin{aligned} \tau_1 &\simeq 4 \cdot 10^{-4} \text{ second} \\ \tau_2 &\simeq 4 \cdot 10^{-3} \text{ second} . \end{aligned}\right\} \qquad (51)$$

(51) must be said to be a sufficient answer to the problem posed in this section.

It is seen that the non-faradayan pulses are much slower than given by (16a), where the time constant is e.g. of the order of magnitude 10^{-10} second.

(50) shows that the process may in the simplest case be very nearly an exponential "relaxation" with a time constant of several milliseconds. If disturbing circumstances are present as e.g. external resistance, displacement of chemical processes ("faradayan pulse") . . . , and if the initial value of J_L is high, the passing off may take a considerable time.

In the next section we shall treat the actual process in the actual set-up by similar reasoning.

IV. The Theory of the Actual Apparatus

Before we turn to the geometrical aspects of the cell with the wire inserted, we shall, in connection with the simple "geometry" in the previous section, treat one obvious generalization, namely that of using a model of the microphases which better corresponds to the refinements used by Macdonald and Barlow [11] of the simple Gouy model. For this purpose we imagine a "rigid" monomolecular layer of water molecules included in each of the microphases between electrolytic solution and metal. Let l_w be the thickness of that layer. If we a priori accept the "equilibrium values" (cf. page 42, small print) also for the dipole layer we shall now, instead of (47), have

$$4\bar{\bar{q}}\left\{\frac{l_w}{2\varepsilon_w}+\frac{1}{\beta\sqrt{(\bar{\bar{q}}^2+\frac{8\alpha\varepsilon_w^2}{\beta})}}\right\}+\frac{h}{\sigma}\bar{\bar{q}}=0 \qquad (52)$$

Let us now calculate the values of β and of

$$\frac{8\alpha\varepsilon_w^2}{\beta}$$

Using the values

$F = 96500$ coulomb mole^{-1}

$\varepsilon_w = 7 \cdot 10^{-10}$ farad m^{-1}

$R = 8.3$ J K^{-1} mole^{-1}

$T = 300$ K

and the definitions of α and β in (38) with 'ε_w' substituted for 'ε_0', one finds in the MKSA (SI) system the values

$$\beta \simeq 40$$

$$\frac{8\alpha\varepsilon_w^2}{\beta} = 8\,RTc\,\varepsilon_w \simeq 1{,}4 \cdot 10^{-5} \cdot c, \text{ (c measured in mole m}^{-3}\text{)}$$

Now the meaning of 'Φ' in (48) must be changed to $\frac{l_w}{\varepsilon_w}+\frac{2}{\beta\sqrt{(\bar{\bar{q}}^2+\frac{8\alpha\varepsilon_w^2}{\beta})}}$

and, according to the inequality in (48) and the calculated values in the MKSA system, one has

$$2 \left(\frac{l_w}{\varepsilon_w} + \frac{2}{40 \sqrt{(q^2 + 1{,}4 \cdot 10^{-5}\ c)}} \right) < 20$$

As l_w is of the order of magnitude 10^{-10} m one finds

$$2 \left(0{,}14 + \frac{2}{\sqrt{1{,}6\ 10^3 q^2 + 2{,}2 \cdot 10^{-2}\ c}} \right) < 20,$$

which shows that the monomolecular layer of water molecules must under our presumptions give a rather modest contribution to the (reciprocal) differential capacity of the microphase. It may therefore be reasonable to leave it out of consideration and to use the simple Gouy model as done in the previous section. Incidentally, if we - as we did above - a priori accept the "equilibrium expression" also for the dipole layer capacity, it is seen that the values τ_1 and τ_2, page 43, are valid independently of the presence of the dipoles.

If in (52) $\frac{l_w}{\varepsilon_w}$ is replaced by $\frac{l}{\varepsilon}$ designating the thickness of an artificial, insulating layer on the electrode plate divided by the dielectric permeability of such a layer, one has the equation for the passing off of the current pulses with artificially insulated electrode plates. It is seen that such an insulating layer does not prevent current pulses to occur, as was indicated on page 13 of [3] , and the formulae set forth may be used to calculate how thin such a layer may be, if it should really alter the passing off. Since the principal idea in the author's work is to avoid insulating the hot wire, we shall not extend the calculations concerning an insulating layer to comprise the more complicated geometrical aspects of the actual measuring cell. It is only noted that for the reasons given in [3] , page 32, the insulating layer should - if one wants to use that modification of the method - be as thin as possible. What has just been said therefore indicates that if monomolecular layers are used for insulation, it should, strictly speaking, be investigated somewhat closer whether the current pulses do not disturb the registrations (at the outset).

We now turn to study the cell with wire retainers that are not plate shaped and with inserted wire. We shall first try to investigate the change from fig. 2 to fig. 3 and the equations (18) connected with the latter figure by using a method similar to that used in the previous section, i.e. by forming certain mean values. Now one half of the wire and its retainer corresponds to one of the electrode plates in the previous section, ions being transported

between the cell halves, as indicated in fig. 2. In the system with electrode plates and the wire removed the voltage will presumably not vary strongly over the electrode plates, and an analogous comment can be put forward concerning the voltage difference through the microphases. But if we insert the wire the voltage difference between metal and solution must, at the later stages of the current pulse, vary considerably along the wire. If this was not so it would be impossible to end up with equilibrium in the solution concurrently with an electric current flowing in the wire: then the "usual" jump condition for the Maxwell equations: namely that the tangential component of $\vec{E}$ is continuous through a boundary surface,would apply. As there are no electromotive forces in the homogeneous macrophases (wire and liquid) this would mean that, according to Ohm's law (12), current could not flow in the wire at the later stages without current also flowing in the liquid. E_z would in both macrophases be equal to $\frac{1}{\sigma}$ multiplied by the current density i_z. However,the chemical composition of the microphases will vary along the wire and this makes the mentioned jump condition invalid. The author has never seen this limitation of the validity of the jump condition mentioned in the literature, but it is very essential in the case studied here. Equilibrium (or almost equilibrium) in the liquid being established simultaneously with a current in the wire could not be understood without fully realizing this point.

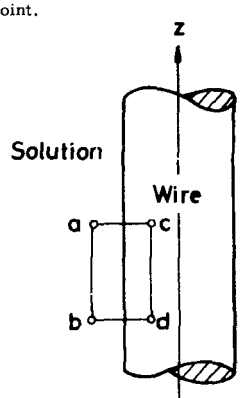


Fig.7

Let us imagine a state where no current flows in the solution but a steady current flows in the wire. We then have from (1):

$$\text{curl}\,\vec{E} = \vec{0} \qquad (53)$$

Let us furthermore consider a small rectangle abdc as indicated in fig. 7. If we integrate (53) over its area we have, according to Stokes's theorem, that the line integral of $\vec{E}$ along abdc is equal to 0. Along ab the contribution to this integral is 0, because there is no $\vec{E}$ field in the homogeneous liquid ($E_z = \frac{i_z}{\sigma} = 0$) since there is no current in it. Along dc the contribution is $\neq 0$. So it follows that the contributions from ca and bd cannot be numerically equal. But this is neither the case if the interfacial layer is inhomogeneous

in the z direction, which can be seen from (29). According to that equation one finds, analogously to the reasoning on page 35

$$-\frac{\partial \mu_+}{\partial r} + FE_r \simeq \frac{i_r}{\sigma} F \quad , \text{ subscript 'r' meaning r component.}$$

If ab and cd are situated in the boundaries of the Gouy layer we have with easily comprehensible symbols, integrating this equation in the r direction

$$\Delta_{ca}\mu_+ - F\int_c^a E_r\,dr \simeq 0 \quad , \quad \Delta_{db}\mu_+ - F\int_d^b E_r\,dr \simeq 0$$

If one considers the surface distributed layers in the metal part of the microphase as limits of difuse distributions one may treat these parts analogously. The reason why the right-hand sides are approximately negligible is that σ is very high and the thickness of the microphase is extremely small. Now, the chemical potentials of ions and electrons are determined by the composition. Hence, if the layer is homogeneous in the z direction, one has $\Delta_{ca}\mu_+ = \Delta_{db}\mu_+$ together with analogous equations in the metal part of the microphase, and the contributions to $\int E_r\,dr$ along ca and bd, fig. 7, are numerically equal. But if the microphase is inhomogeneous in the z directions the said contributions may be different, as they must be.

Now what was set forth immediately above was strictly speaking a digression. In the present case one can define a mean value $\bar{\delta}$ of the voltage difference between solution and metal taken over one half of the wire and its retainer by an expression analogous to (33):

$$\bar{\delta} = \bar{\varphi}_O - \bar{\varphi}_M \quad , \tag{54}$$

The only principal difference from the former case is that the diffuse layers are now curved. In (54) $\bar{\varphi}_O$ and $\bar{\varphi}_M$ are mean values (of φ) over the wirehalf considered and its retainer, and because the layer is so extremely thin it is irrelevant if we form the mean values over the outer boundary (index 'O') or the inner one (index 'M').

Let us now confine ourselves to investigating the later, slower stages of the current pulses so that we may put $\frac{\partial \vec{A}}{\partial t} = \vec{0}$ in (12). This is done merely for the sake of convenience because only integrated forms of Ohm's law will be used, and putting $\frac{\partial \vec{A}}{\partial t} = \vec{0}$ from the outset means in the following derivations, although it is not correct, that it is not necessary constantly to point out that it is only in the integrated form induction may be neglected.

In the following the coordinate system is the "usual" polar one with the z axis along the wire axis. It is assumed that besides the rotational symmetry of the lines of current round the z axis the $\vec{i}$ field also shows symmetry with

respect to the middle cross section of the cell, OO fig. 8. This figure shows an instantaneous, electric streamline tube, originating in an infinitesimal area dA of the wire surface and ending in a corresponding infinitesimal area dA congruent with the former, situated symmetrical to it. This assumption of symmetry will be taken as self-evident during the following considerations.

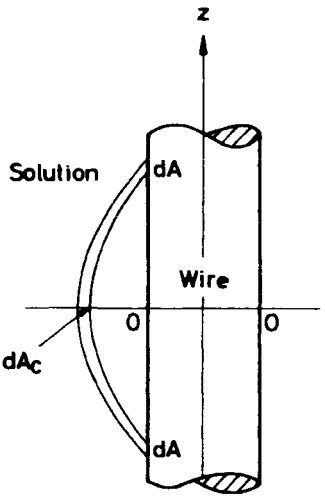


Fig.8

Now, in order to justify the model with lumped parameters, fig. 3 in detail and the equations (18) connected with it, one must stipulate definitions of the current J_L in the liquid and the resistance R_L of the liquid. These definitions are not given beforehand because the electric streamlines in fig. 8 are curved.

Since we have put $\vec{i} = -\sigma \operatorname{grad} \varphi$ (and σ = const.) in the bulk of the liquid one has curl $\vec{i} = \vec{0}$ there, and therefore there exists (at every t) a system of orthogonal surfaces to the streamlines. If dS is the area element of such a surface and $|\vec{i}| = i$, a natural definition of J_L would be $J_L = \int i dS$ taken over the surface.

But, because of the radial current to and from the wire halves, J_L defined in this way is dependent on the orthogonal surface considered. At the middle cross section the orthogonal surface is plane - namely the cross section itself - and $J_L = J_L^{OO}$ = the whole current coming from or flowing to a wire half ("plus" its retainer). This fact makes it natural to define

$$J_L = J_L^{OO} .$$

Furthermore the fact that the current is not one-dimensional in the z direction makes it problematic what 'R_L' should be taken to mean. In the considerations in [3] using the model with lumped parameters R_L was defined as

if the current were directed only in the z direction, i.e. the definition

$$R_L = \frac{h}{\sigma A_S} \quad , \text{ where}$$

h = length of the cell

A_S = cross sectional area of the bulk of the solution column

σ = specific conductivity of the solution

was used. We shall stipulate to use this definition here too.

If one integrates Ohm's law for the z direction, $i_z = -\sigma \frac{\partial \varphi}{\partial z}$, over A_S one arrives at

$$\int_{A_S} i_z \, dA_S = -A_S \sigma \frac{\partial}{\partial z} \tilde{\varphi}_S \quad ,$$

where $\tilde{\varphi}_S$ is the mean value of φ in the solution over A_S. To put the integral on the left-hand side of this equation exactly equal to J_L^{OO}, considering it to be independent of z, is not correct. Thus the said integral vanishes at the ends of the liquid column and is exactly $= J_L^{OO}$ at the middle cross section OO. But it may be a permissible approximation in the present context to put

$$\int_{A_S} i_z \, dA_S \simeq J_L^{OO} = J_L, \text{ independent of z.}$$

To do this is tantamount to put $\frac{\partial}{\partial z} \tilde{\varphi}_S$ approximately independent of z, or in other words to put

$$\frac{\partial}{\partial z} \tilde{\varphi}_S = \frac{\Delta \tilde{\varphi}_S}{h} \quad ,$$

where $\Delta \tilde{\varphi}_S$ is the difference of the $\tilde{\varphi}_S$-values at the ends of the liquid column. If the said approximation is permissible one thus has

$$\Delta \tilde{\varphi}_S \simeq \frac{h}{\sigma A_S} J_L^{OO} = R_L J_L^{OO} \quad .$$

Whether this equation is reasonable can be judged by integrating the Laplace*) equation for φ in the bulk of the solution over A_S. Doing this, and putting $r_c - r_w \simeq r_c$, where r_c and r_w are the radii of cell and wire, respectively, one arrives at

---

*) The macrophages are electroneutral

$$\frac{\partial^2 \tilde{\varphi}_S}{\partial z^2} \simeq - \frac{2\, r_w}{r_c^2} \frac{(i_r)_o}{\sigma} \,.$$

$(i_r)_o$ is the r component of $\vec{i}$ at the boundary between the bulk of the solution and the microphase around the wire. Here we have neglected the r component of $\vec{i}$ at the boundary of the microphase round the glass wall of the cell. To do this must be reasonable, but $(i_r)_o$ is certainly $\neq 0$, ions being transported between the bulk of the solution and the microphase round the wire. Nevertheless, at low applied voltages $(i_r)_o$ is not extremely high if r_w is not quite extremely small, and $r_c \gg r_w$. Furthermore σ is high and hence it seems permissible to put

$$\frac{\partial^2 \tilde{\varphi}_S}{\partial z^2} \simeq 0 \,,$$

or, according to the above and neglecting the charge transport in the microphases as compared to the transport through the bulk,

$$\Delta\tilde{\varphi}_S \simeq R_L J_L^{oo} \,, \tag{55}$$

Having now accepted this*) it is elementary to see that approximately

$$\Delta\tilde{\varphi}_S = 2\, \Delta\bar{\tilde{\varphi}}_S \tag{56}$$

where $\Delta\bar{\tilde{\varphi}}_S$ is the difference of the mean values of $\tilde{\varphi}_S$ over the curved surfaces of the wire halves ("plus" their wire retainers). Furthermore, if r_w is not extremely small, one finds by an analogous procedure - i.e. by forming the mean value $\tilde{\varphi}_w$ over the wire cross section and integrating the Laplace equation for φ in the wire macrophase - on account of the extremely high specific conductivity of the wire material

$$\Delta\varphi_c = \Delta\tilde{\varphi}_w \simeq 2\, \Delta\bar{\tilde{\varphi}}_w \tag{57}$$

where '$\Delta\varphi_c$' means the voltage applied to the cell and the other symbols have meanings analogous to the symbols in (56).

From (55), (56) and (57) one has

$$\Delta\varphi_c - R_L J_L^{oo} \simeq 2\, (\Delta\bar{\tilde{\varphi}}_w - \Delta\bar{\tilde{\varphi}}_S) \tag{58}$$

*) i.e. $\frac{\partial^2 \tilde{\varphi}_S}{\partial z^2} \simeq 0$

Under our assumption (low applied voltage) the profiles of φ in the r direction in the main parts of both macrophases may be considered fairly flat. We may therefore put $\tilde{\varphi}_w$ and $\tilde{\varphi}_S$ approximately equal to the φ-values at the wire surface at the same z values. Hence one has from (58)

$$\Delta\varphi_c - R_L J_L^{oo} \simeq 2\,(\Delta\bar{\varphi}_w - \Delta\bar{\varphi}_S) = 2\,\Delta\,(\bar{\varphi}_w - \bar{\varphi}_S)$$

where the bars mean that mean values (of φ itself, not of $\tilde{\varphi}$) are formed over the curved surface of the wire halves and 'Δ' means difference. Finally by aid of (54) one finds

$$\Delta\varphi_c \simeq R_L J_L^{oo} + 2\,\Delta\,\bar{\delta} \tag{59}$$

where the last term on the right-hand side can be interpreted as the counter electromotive force $\mathcal{E}$ in the upper formula of (18). In other words, when J_L in this formula is specified to be J_L^{oo} the formula is approximately valid:

$$\Delta\varphi_c \simeq R_L J_L^{oo} + \mathcal{E}\ . \tag{59a}$$

If J_w^{oo} = the current in the middle cross section of the wire, it is also easy to see that the lower formula of (18) is valid in the form

$$\Delta\varphi_c \simeq R_w J_w^{oo}\ . \tag{60}$$

We may of course always make the formulae (59) and (60) exactly valid by adding two factors f_1 and f_2 defined through the formulae

$$f_1\ \Delta\varphi_c = R_L J_L^{oo} + 2\,\Delta\,\bar{\delta}$$

$$f_2\ \Delta\varphi_c = R_w J_w^{oo}$$

themselves. In these formulae f_1 and f_2 are dependent on time and it would be an intricate mathematical-physical problem to find f_1 and f_2, i.e. to make these formulae more than definitions of f_1 and f_2. However, as seen above, under the assumption of low applied voltages $\Delta\varphi_c$, it is reasonable to put $f_1 \simeq 1$ and $f_2 \simeq 1$, and we shall adopt this in the following. Furthermore, the analysis in [3] using (18) had so ample a margin that moderate deviations of the f's from unity play no role for the validity of its results.

We are now in a position to study the non-faradayan current pulses in the actual apparatus. In the previous section a simplified system with the electrodes formed as plates and the wire removed was studied. An essential point of that investigation was the integration of the Poisson equation "through" the microphases at the electrodes, carried out on pages 33-34 and ending up with (28). Quite an analogous procedure may be followed here, although the equations are a little more complicated because the microphases along the wirehalves are curved. Nevertheless the extremely small value of the thickness of these phases entails results that are quite analogous to those obtained loc cit in the previous section: Let $\bar{\rho}$ be the mean value of ρ over a cylindrical surface with axis in the z direction and situated at an arbitrary r in the curved Gouy layer round a wirehalf. Let, moreover, $\bar{q}$ be defined by

$$\bar{q} = \int_{O}^{M} \bar{\rho}\, dr$$

the integration being performed through the Gouy layer (indices 'O' and 'M' indicate this). One then ends up with

$$(\bar{\varphi}_r)_O - (\bar{\varphi}_r)_M = -\frac{\bar{q}}{\varepsilon_w} \qquad (61)$$

Here index 'r' indicates differentiation with respect to r. (61) has the same form as (28) and it turns out that we may reason in the same way as we did when (45) was derived. We only have to substitute 'r' for 'z' in that derivation. From (59) and (45) then follows

$$\dot{\Delta\varphi}_c = R_L \dot{J}_L^{oo} + \frac{8\dot{\bar{q}}}{\beta\sqrt{(\bar{q}^2 + \frac{8\alpha}{\beta}\varepsilon_w)}}$$

a dot meaning, as usual, differentiation with respect to time. Hence, if we ignore external resistances in the leads to the cell and consider the terminal voltage of the source cell constant we have

$$R_L \dot{J}_L^{oo} + \frac{8\dot{\bar{q}}}{\beta\sqrt{(\bar{q}^2 + \frac{8\alpha}{\beta}\varepsilon_w)}} = 0$$

in this equation one can evidently put

$$J_L^{oo} = |\dot{\bar{q}}\,\frac{A_w}{2}|\ .$$

where A_w = the curved surface of the wire and the wire retainers. Moreover, according to the above,

$$R_L = \frac{h}{\sigma A_S} ,$$

where A_S is almost equal to the cross section A_c of the cell. Hence, one finds for the non-faradayan pulse in the actual cell

$$\frac{4 \dot{\bar{q}}}{\beta \sqrt{(\bar{q}^2 + \frac{8\alpha}{\beta} \varepsilon_w)}} + \frac{A_w}{4 A_c} \cdot \frac{h}{\sigma} \dot{\bar{q}} = 0 . \qquad (62)$$

It is seen by comparison with (47), representing what was called 'the pure phenomenon' that a "form factor" $\frac{A_w}{4 A_c}$ appears when the wire is inserted. On pages 42-43 the solution of the equation for $J_L = J_L^{oo}$ corresponding to (47) was approximated by exponential functions. If one follows the same procedure with regard to (62) it is seen that seemingly a thin wire (small A_w) and a thick cell (high A_c) will be advantageous. This seems to contradict the idea of the modification of the "classical" set-up used by the author in [3] in order to make the method applicable to measurements on electrolytic solutions. In that modification the change from the "classical" very thin wire to a "thick" wire was extremely important.

But it should be remembered that in (62) A_w includes the surface areas of the retainers, and looking at the sketch of the cell fig. 9 , where all dimensions are given in mm, it is seen that, as a matter of fact, also the thick wire contributes only modestly to A_w. A_w is mainly determined by the retainers, which have been given rather large cross sections for the reasons mentioned in [2], page 26. So according to (62) there is no really important difference in the time constant of the exponential functions giving the 2 "limits" of the solution (cf section III, page 43) for the classical and for the modified set-up when the cells have equal cross sections. If τ is the time constant of the said exponential curves we have for each of these limits - omitting the index 'oo' -

$$J_L = (J_L)_o \; e^{-\frac{t}{\tau}} , \qquad (63)$$

where $(J_L)_o$ is the initial value of J_L.

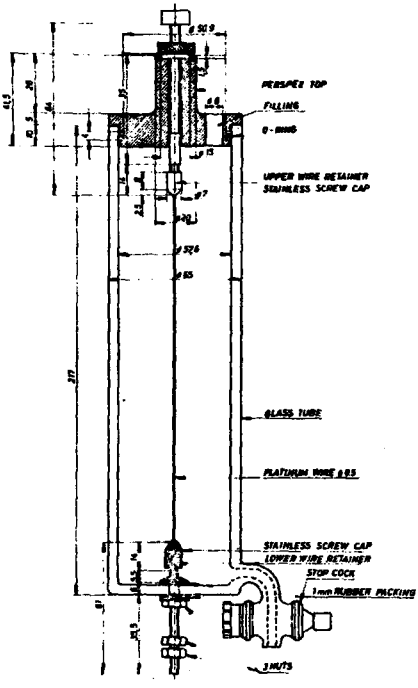

PERSPEX TOP
FILLING
O - RING
UPPER WIRE RETAINER
STAINLESS SCREW CAP
GLASS TUBE
PLATINUM WIRE ø 0.5
STAINLESS SCREW CAP
LOWER WIRE RETAINER
STOP COCK
1 mm RUBBER PACKING
3 NUTS

Fig 9

Let us now try to estimate the most favourable value $\tau = \tau_1$ and the most unfavourable value $\tau = \tau_2$ in (63) for the actual apparatus. For "the pure phenomenon" we found on page 43

$$\left.\begin{aligned} \tau_1 &= 4 \cdot 10^{-4} \text{ second} \\ \tau_2 &= 4 \cdot 10^{-3} \text{ second.} \end{aligned}\right\}$$

For the actual cell we have therefore according to (62)

$$\left.\begin{aligned} \tau_1 &= \frac{A_w}{A_c}\, 10^{-4} \text{ second} \\ \tau_2 &= \frac{A_w}{A_c} \cdot 10^{-3} \text{ second} \end{aligned}\right\} \qquad (64)$$

In the modified cell the radius of the wire is 0.25 mm and its length about 170 mm. Hence its curved surface is $\simeq$ 260 mm. The value of A_w depends upon the design of the retainers and on the height to which the cell is filled. In the following we shall take $A_w \simeq 1000$ mm^2 for the modified and $A_w \simeq 800$ mm^2 for the classical set-up. From fig. 9 it is seen that these rounded values are reasonable (although, maybe, a little high for the cell actually used). In both apparatuses the radius of the cross section of the cell was 30 mm, i.e. $A_c \simeq 2700$ mm^2. For the order of magnitude of the τ's one therefore has, according to (64), for both cells

$$\left.\begin{aligned} \tau_1 &= 3 \cdot 10^{-5} \text{ second} \\ \tau_2 &= 3 \cdot 10^{-4} \text{ second} \end{aligned}\right\} \qquad (65)$$

and it is seen that the passing off of the pulse is favourably influenced by "the geometry" of the apparatus as compared to "the pure case".

On page 27 it was mentioned that the analysis in [3] presupposes that "displacement currents" may be neglected when using the "model" fig. 3. The said analysis is based on the following equations

$$\left.\begin{aligned} \Delta\varphi_c &= R_L J_L + \mathcal{E} \\ \Delta\varphi_c &= R_w J_w \\ \Delta\varphi_c &= R_c J_c \\ J_c &= J_L + J_w \end{aligned}\right\} \qquad (66)$$

The two upper equations were mentioned on page 26 and they are justified by (59a) and (60), if J_L and J_w are taken to be J_L^{oo} and J_w^{oo} respectively. In the third equation R_c is the total resistance of the cell and J_c the current flowing to it. The validity of the last equation of (66) is dependent on the permissibility of the said presumption concerning displacement currents.

We are now in a position to study also that presumption a little closer*). Using the symbols of fig. 3 (and of [3], page 14) one has

$$J^* + \frac{\varepsilon^*}{\sigma^*}\frac{dJ^*}{dt} = J_L + \frac{\varepsilon}{\sigma}\frac{dJ_L}{dt} \quad , \tag{67}$$

and the equation '$J_c = J_L + J_w$' in (66) is equivalent to the assumption that (67) may approximately be written

$$J^* = J_L \quad . \tag{67a}$$

Hence, if (67a) can be justified, (66) has been justified, and the model fig. 3 is approximately correct (with $J_L = J_L^{oo}$ and $J_w = J_w^{oo}$). In (67) the ε's and the σ's are dielectric permeabilities and specific conductivities respectively and asterisks refer to the metal (the wire). ε and σ are values in the liquid. In the appendix of [3] an example of the order of magnitude of $\frac{\varepsilon}{\sigma}$ was given, namely for a 1 N aqueous KCl solution at 25°. For such a solution it was found that

$$\frac{\varepsilon}{\sigma} \simeq 10^{-10} \text{ second}$$

i.e.

$$\left|\frac{\varepsilon}{\sigma}\frac{\dot{J}_L}{J_L}\right| = 10^{-10}\left|\frac{\dot{J}_L}{J_L}\right| \quad . \tag{68}$$

Now (62) can, by introducing Φ (or ϕ) as done on page 42, be written

$$2\,\Phi\,J_L + \frac{A_w}{4\,A_c}\frac{h}{\sigma}\dot{J}_L = 0 \quad , \tag{69}$$

i.e.

$$\left|\frac{\dot{J}_L}{J_L}\right| = \frac{2\,\Phi}{\frac{A_w}{4\,A_c}\frac{h}{\sigma}} < \frac{40}{1.2 \cdot 10^{-3}} \text{ second}^{-1} \quad ,$$

because $2 < \Phi < 20$ in the MKSA system. From (68) it then follows that

$$\left|\frac{\varepsilon}{\sigma}\frac{\dot{J}_L}{J_L}\right| < \frac{4}{1.2}\,10^{-6} \quad ,$$

and it is seen that $\frac{\varepsilon}{\sigma}\dot{J}_L$ in (67) can with extremely good approximation be neglected:

$$J^* + \frac{\varepsilon^*}{\sigma^*}\dot{J}^* = J_L \quad . \tag{67b}$$

---

*) To do this is important because using the equation '$J_c = J_L + J_w$' is tantamount to ignoring the total charge in the interfacial layers round the wire halves during the pulse. (cf page 38, where it was assumed that $|\Delta\overline{q}|$ is small).

If one puts the right-hand side of (67) equal to Q and $\frac{\varepsilon^*}{\sigma^*} = \tau^*$, (67) can be written

$$\dot{J}^* + \frac{1}{\tau^*} J^* = \frac{Q}{\tau^*} \quad ,$$

which is solved by

$$J^* = e^{-\frac{t}{\tau^*}} \left\{ \int_0^t e^{\frac{t}{\tau^*}} \frac{Q}{\tau^*} dt + J_o^* \right\} ,$$

where $J_o^* = J^*$'s initial value. Since $e^{\frac{t}{\tau^*}} > 0$ and, according to the above, also $Q > 0$, the integral

$$\int_0^t e^{\frac{t}{\tau^*}} Q \, dt$$

can by aid of a well-known mean value theorem be written as

$$Q_m \cdot \int_0^t e^{\frac{t}{\tau^*}} dt \quad ,$$

where Q_m is a "mean value" of Q. Hence

$$J^* = Q_m (1 - e^{-\frac{t}{\tau^*}}) + J_o^* e^{-\frac{t}{\tau^*}} \quad . \tag{70}$$

Furthermore, if (70) is multiplied by τ^* and differentiated with respect to time it is found, Q_m and $\dot{Q}_M$ being finite, that $\tau^* \dot{J}^* = \frac{\varepsilon^*}{\sigma^*} \dot{J}^* \to 0$ when $\tau^* \to 0$. The left-hand side of (67b) will consequently $\to J^*$ when $\tau^* \to 0$. Now σ^* is extremely high (σ^* for Pt is $\simeq 10^7\ \Omega^{-1}\ m^{-1}$, which is certainly high as compared e.g. to σ for the above-mentioned K Cl solution $\simeq 10\ \Omega^{-1}\ m^{-1}$). It must therefore be reasonable to consider the actual case being near to the limiting case $\sigma^* \to \infty$, i.e. $\tau^* \to 0$ and to consider (67a) justified. Thus the use of the model fig. 3 and the equations (66) connected with it is established for the case that there are no resistances in the leads to the cell, ((69) is built upon that presumption). Before the final investigation of the modification is undertaken we must therefore investigate if the τ's in (65) are altered essentially by taking "external" resistances in the circuit into account.

Let us for the sake of simplicity ignore the fact that the actual circuit is ramified (the cell is a component of a Wheatstone bridge). The result of the circuit analysis is then altered to

$$\Delta\varphi_c + RJ_c = P \quad , \tag{71}$$

where R is the external resistance in the leads and P, as usual, the terminal voltage of the source cell. Let us furthermore assume that the τ's in (65) are not altered so much that the support of (66) given above is invalid. This assumption is confirmed later. Considering P constant one then finds by aid of (66) and (71)

$$\Delta\dot{\varphi}_c + R_w \frac{R}{R + R_w} \dot{J}_L = 0 \quad ,$$

or

$$\left.\begin{aligned} &\Delta\dot{\varphi}_c + \rho R_w \dot{J}_L = 0 \\ &\rho = \frac{R}{R + R_w} \quad . \end{aligned}\right\} \tag{72}$$

In (72) $\Delta\dot{\varphi}_c$ is, according to pages 42 - where Φ was defined - and 52, given by

$$\Delta\dot{\varphi}_c = R_L \dot{J}_L + 4\,\Phi\,\dot{\bar{q}} = R_L \dot{J}_L + 8\,\frac{\Phi}{A_w} J_L \quad , \tag{73}$$

so that (72) gives

$$\frac{8}{A_w}\,\Phi J_L + (R_L + \rho R_w)\,\dot{J}_L = 0 \quad . \tag{74}$$

During a blank experiment or a sufficiently fast passing off of the pulse in a main experiment (λ-measurement) R_w *is not* altered by heating of the wire, i.e. R_w = const. One thus has from (74) for the altered τ's in (63)

$$\tau = \frac{A_w}{8\,\Phi}\,(R_L + \rho R_w) = \tau_o + \frac{A_w}{8\,\Phi}\,\rho R_w \quad ,$$

where 'τ_o' represents the values found above for the case $\rho = 0$, namely (65). This gives

$$\left.\begin{aligned} \tau_1 &= 3 \cdot 10^{-5} + \frac{A_w}{160}\,\rho R_w \text{ second} \\ \tau_2 &= 3 \cdot 10^{-4} + \frac{A_w}{16}\,\rho R_w \text{ second} \quad , \end{aligned}\right\} \tag{75}$$

because $2 < \Phi < 20$ in the MKSA system. In (75) A_w is measured in m^2 and R_w in Ω.

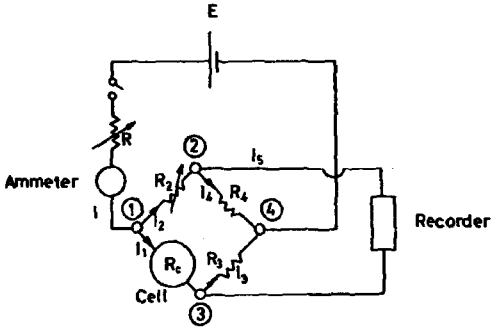

E
R
Ammeter
I
2
I_5
R_2
I_4
R_4
1
4
I_2
I_1
R_c
R_3
I_3
Cell
3
Recorder

Fig.10

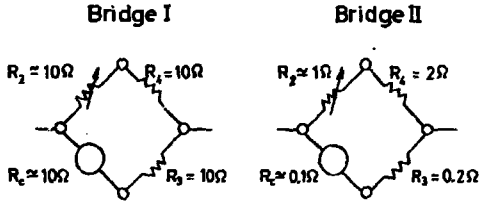

Bridge I
Bridge II
$R_2 = 10\Omega$
$R_4 = 10\Omega$
$R_c \simeq 10\Omega$
$R_3 = 10\Omega$
$R_2 \simeq 1\Omega$
$R_4 = 2\Omega$
$R_c \simeq 0.1\Omega$
$R_3 = 0.2\Omega$

Fig. 11

In the "classical", unmodified set-up R_w was, according to [3], page 21, 16 Ω so that

$$\left.\begin{aligned} \tau_1 &= 3 \cdot 10^{-5} + \rho \cdot 800 \cdot 10^{-7} \text{ second} \\ \tau_2 &= 3 \cdot 10^{-4} + \rho \cdot 800 \cdot 10^{-6} \text{ second} \end{aligned}\right\} .$$

The actual (ramified) circuit is shown on fig. 10 and an example of a "classical" bridge is shown as "bridge I" on fig. 11. In that figure R_c should as mentioned be changed to be 16 Ω (valid when the pulse has faded out, and $R_c = R_w$). In the classical circuit E on fig. 10 was 12 volt and $R \simeq 50$ Ω. For an unramified circuit we have

$$\rho = \frac{R}{R + R_w} \simeq 0.8 ,$$

if $R = 50$ Ω and $R_w = 16$ Ω. If one carries out a more refined analysis - which is a little lengthy but quite straight forward - taking the ramification into account one finds $\rho \simeq 0.6$ in (75) and hence

$$\left.\begin{aligned} \tau_1 &\simeq 8 \cdot 10^{-5} \text{ second} \\ \tau_2 &\simeq 8 \cdot 10^{-4} \text{ second} \end{aligned}\right\} \quad \text{"classical" set-up.} \qquad (76)$$

The modified bridge is shown as "bridge II" on fig. 11. As before E = 12 volt, but now $R \simeq 3$ Ω. Both for an unramified and for the actual, ramified circuit one then finds $\rho \simeq 1$ in (75). Since $R_w = 0.1$ Ω one finally arrives at

$$\left.\begin{aligned} \tau_1 &\simeq 3 \cdot 10^{-5} \text{ second} \\ \tau_2 &\simeq 3 \cdot 10^{-4} \text{ second} \end{aligned}\right\} \quad \text{modified set-up.} \qquad (77)$$

It thus turns out that the resistances in the leads of the circuit do not change the τ's in the modified set-up but makes them more unfavourable by a factor $\simeq 3$ in the classical set-up.

Form the above it is seen that a comparison between the classical and the modified set-up can be made using the model fig. 3, its corresponding equations (66), the "limits" τ_1 and τ_2 given by (76) and (77) and the equation (73).

From (66) is found for the resistance of the cell, R_c (cf [3], pages 15-16)

$$\left.\begin{aligned} R_c &= \frac{R_w}{1 + f\left(1 - \frac{\mathcal{E}}{\Delta\varphi_c}\right)} \\ f &= \frac{R_w}{R_L} \end{aligned}\right\} \qquad (78)$$

Since $\mathcal{E}$ is the counter electromotive force we have at t = 0 (when the current is switched on) $\mathcal{E} = 0$ and when the current pulse in the cell has practically died out $\mathcal{E} \simeq \Delta\varphi_c$, $J_L \simeq 0$ and $R_c = R_w$. The question is how fast the latter state is reached.

Integrating (73) with respect to time one finds

$$\Delta\varphi_c = R_L J_L + \frac{\delta}{A_w} \int \Phi J_L \, dt + \text{const} \quad , \tag{79}$$

and from (66)

$$\mathcal{E} = \frac{\delta}{A_w} \int \Phi J_L \, dt + \text{const} \quad . \tag{80}$$

Since the exact solution of the equation for J_L was not given we can study the "most unfavourable limiting case" corresponding to $\Phi = 2$ in the MKSA system and

$$J_L = (J_L)_0 \, e^{-\frac{t}{\tau_2}} \quad , \quad \text{i.e.} \quad \int J_L \, dt = -\tau_2 J_L \quad .$$

Substituted into (79) and (80) this gives

$$\left.\begin{aligned} \Delta\varphi_c &= R_L J_L - \frac{16}{A_w} \tau_2 J_L + \Delta\varphi_\infty \\ \mathcal{E} &= -\frac{16}{A_w} \tau_2 J_L + \Delta\varphi_\infty \\ J_L &= (J_L)_0 \, e^{-\frac{t}{\tau_2}} \quad , \end{aligned}\right\} \tag{81}$$

where $\Delta\varphi_\infty = \Delta\varphi_c$ at $t = \infty$.

In (81) it is convenient to introduce the abbreviations

$$\left.\begin{aligned} T &= \frac{16}{A_w} \tau_2 \\ R_L - T &= S \quad , \end{aligned}\right\} \tag{82}$$

so that from (81) one has

$$\frac{\mathcal{E}}{\Delta\varphi_c} = \frac{\Delta\varphi_\infty - T J_L}{\Delta\varphi_\infty + S J_L} \quad , \tag{83}$$

and from (78)

$$R_c = R_w \frac{\Delta\varphi_\infty + S\, J_L}{(R_L \cdot T + S)\, J_L + \Delta\varphi_\infty} \quad . \tag{84}$$

Now, (78) shows that at $t = 0$, when $\mathcal{E} = 0$,

$$R_c = R_c^o = \frac{R_w}{T + T} \quad ,$$

so that according to (84)

$$\frac{1}{T + T} = \frac{\Delta\varphi_\infty + S(J_L)_o}{(R_L T + S)(J_L)_o + \Delta\varphi_\infty} \quad ,$$

from which follows

$$(J_L)_o = \frac{\Delta\varphi_\infty}{T} \quad . \tag{85}$$

From (82), (76) and (77) one finds

"classical" set-up :	modified set-up :
($A_w = 800\ mm^2$, $R_L = 5\ \Omega$)	($A_w = 1000\ mm^2$, $R_L = 5\ \Omega$)
$T = 16\ \Omega$	$T = 4.8\ \Omega$
$S = -11\ \Omega$	$S = 0.2\ \Omega$.

In a blank experiment R_w is constant and $\Delta\varphi_\infty = R_w J_w^\infty$ where J_w^∞ is the final current in the wire = the final current fed to the cell. In the classical set-up J_w^∞ is of the order of magnitude 0.1 A and in the modified $J_w^\infty \simeq 3.5$ A. Hence from (85)

"classical" set-up :	modified set-up :
$(J_L)_o = \frac{16 \cdot 0.1}{16} = 0.1\ A$	$(J_L)_o = \frac{0.1 \cdot 3.5}{4.8} \simeq 0.07\ A$
$J_L = 0.1 \cdot e^{-1.3 \cdot 10^3 t}\ A$	$J_L = 0.07\, e^{-3.3 \cdot 10^3 t}\ A$

where 'J_L' refers to "the most unfavourable limiting case". By the modification $(J_L)_o$ has thus been improved $\frac{10}{7}$ times and τ_2 $\frac{3.3}{1.3}$ times. But if one considers only these expressions for J_L, the improvement does not seem to be very drastic. One must study its importance in connection with R_c which is the (indirectly) registered quantity.

From (84), (85) and the last equation of (81) one finds

$$\frac{R_w - R_c}{R_w} = \frac{e^{-\frac{t}{\tau_2}}}{\frac{T}{R_w} + (1 + \frac{S}{R_w}) e^{-\frac{t}{\tau_2}}} , \qquad (86)$$

where $f = \frac{R_w}{R_L}$ has been used. From (86) and the above data follows:

classical set-up :

$$\frac{R_w - R_c}{R_w} = \frac{e^{-1.3 \cdot 10^3 t}}{1 + 0.3\, e^{-1.3 \cdot 10^3 t}} \cdot (87)$$

modified set-up :

$$\frac{R_w - R_c}{R_w} = \frac{e^{-3.3 \cdot 10^3 t}}{48 + 3\, e^{-3.3 \cdot 10^3 t}} \cdot (87a)$$

A necessary condition for making the method work is that the deviation of the registered R_c from its final value R_w will be so small that it can be neglected fast enough, i. e. before R_w is changed appreciably owing to heating. If R_c changes simultaneously owing to the pulse and owing to the heating the changes interfere and cannot be separated. They can according to (78) not even be superposed so that one cannot "subtract" the diagrams of blank experiments from diagrams of main experiments in order to obtain "true" diagrams.

In order to be on the safe side we may e. g. stipulate that

$$\frac{R_w - R_c}{R_w} = 10^{-4} ,$$

before R_w changes registrably owing to heating. This will be in agreement with the improved accuracy which was the result of introducing full automation (cf page 6). From (87) and (87a) it is found that this condition is fulfilled at

$t = 7.1 \cdot 10^{-3}$ second in the classical set-up
and $t = 1.6 \cdot 10^{-3}$ second in the modified set-up.

Hence the set-up has with respect to the said condition been improved about 4 times as far as non-faradayan pulses are concerned. But it is also seen that if there were no other requirements to be fulfilled the modification was not necessary at all if one waits e. g. $10 \cdot 10^{-3}$ second before using the registrations: From a diagram registered with the platinum wire inserted and with pure water in the cell, which is shown in [3], page 44, it is seen that the change in R_w owing to heating cannot be registered during that time interval in the modified set-up and the same was the case in the classical set -up. However, although it was stressed on page 10 that non-faradayan pulses

do occur it was also said that one cannot always assume such pulses. From the above it follows e.g. that the characteristic case shown on fig. 4 - a blank experiment on a NaCl solution in the classical set-up - cannot have been faradayan. On fig. 4 the voltage axis has its positive direction downwards. According to the above one has at $t = 7.1 \cdot 10^{-3}$ second that the remaining change of R_c is

$$R_w - R_c = R_w \cdot 10^{-4} = 16 \cdot 10^{-4}\ \Omega$$

in the classical set-up if the pulse is non-faradayan. Now, according to the circuit analysis in [2], page 41 one has for the registered voltage φ

$$\varphi = J \frac{R_4 (R_c - R_c^o)}{\Sigma + (R_c - R_c^o)}$$

where 'R_4' refers to figures 10-11, J = the current fed to the bridge, and Σ = the sum of R_c^o and the other resistances in the Wheatstone bridge.

From this expression and $R_w - R_c = 10^{-4} R_w$ at $t = 7.1 \cdot 10^{-3}$ second it is easy to see that, if the pulse were non-faradayan, the registered voltage could only change by 0.05 mv from $t = 7.1 \cdot 10^{-3}$ second to $t = \infty$ (J being $\simeq 0.1$ A, $R_4 = 10\ \Omega$ and $R_w = 16\ \Omega$). The pulse can therefore not have been non-faradayan, at least not non-faradayan in accordance with the calculations made above, assuming small applied voltages and the validity of the laws of diluted solutions.

Hence it turns out that one must reckon with very significant delays of the approach of R_c to R_w relative to the approaches given by (87) and (87a). The approach may evidently be delayed to go on slowly through e.g. the whole period of measurement or even a larger time interval. Putting t = 0 in (87) and (87a) one finds for the whole change of R_c, $\Delta\tilde{R}_c$, during a blank experiment, which is imagined continued to $t = \infty$:

classical set-up :	modified set-up :
$\Delta\tilde{R}_c = 16 \frac{1}{1.3}\ \Omega$	$\Delta\tilde{R}_c = 0.1 \frac{1}{51}\ \Omega$
$\Delta\tilde{R}_c \simeq 12\ \Omega$	$\Delta\tilde{R}_c \simeq 2 \cdot 10^{-3}\ \Omega$

which is in agreement with values given in [3], page 21 when the approximations made here are taken into account.

Here we see the kernel of the modification: $\Delta\tilde{R}_c$ has been diminished $6 \cdot 10^3$ times, but the total change of R_w owing to heating during measurements, ΔR_w, - with which $\Delta\tilde{R}_c$ interfers, is according to [3], page 21, about $7.4 \cdot 10^{-2}\,\Omega$ for the classical and about $1.2 \cdot 10^{-3}\,\Omega$ for the modified set-up, i.e. it is only diminished about 60 times. For the classical set-up we have

$$\frac{\Delta\tilde{R}_c}{\Delta R_w} = \frac{12}{7.4 \cdot 10^{-2}} \simeq 160$$

and for the modified

$$\frac{\Delta\tilde{R}_c}{\Delta R_w} = \frac{2}{1.2} \simeq 1.7 \ .$$

True, $\Delta\tilde{R}_c$ and ΔR_w are of the same order of magnitude in the modified set-up but, as it has been mentioned before, all pulses must commence as non-faradayan pulses, and these are, according to the above, extremely fast so that the cell runs through a high fraction of $\Delta\tilde{R}_c$ nearly instantaneously, before the faradayan delay sets in. Since $\Delta\tilde{R}_c \simeq 2 \cdot 10^{-3}\,\Omega$ in the modified set-up and the rate of the initial non-faradayan part of the pulse is according to the above even improved 4-5 times, but $\Delta\tilde{R}_c \simeq 12\,\Omega$ in the classical there is an overwhelming probability of having blank curves as fig. 5 in the modified and blank curves as fig. 4 in the classical set-up when the pulses are "faradayan". In the last-mentioned set-up one may even expect that it is necessary to diminish the sensitivity of the recorder in order to keep the registrations during measurements on the paper. As seen from fig. 4 this is the case e.g. for a 0.5 N Na Cl solution. Diminishing the sensitivity of the recorder 10 times as on fig. 4 furthermore involves that the contribution to the change of R_c through heating of the wire - which is sought - is now only influencing the recordings to a small extent so that even if one could subtract "blank curves" from "measurement curves" to obtain "true" curves the result would be too "small" to be useful.

Since the author has had no possibility of studying theoretically faradayan complications in detail, the blank experiments must, however, still be considered a necessary part of the modification if one wants to be on the safe side.

To sum up: In the previous section "the pure case" of a (mainly one -dimensional) non-faradayan pulse was studied and the differential equation for its development in time was derived. Changing in this section to the study of non-faradayan pulses in the actual apparatus it is found that one of the coefficients of this equation is altered by a certain "form factor". By aid of the altered equation and certain other considerations it was possible to justify the analysis in [3] which makes use of a model with "lumped electrical parameters". That analysis is, in its turn, fundamental to the justification of the modified method and the results obtained with it.

It has been shown that non-faradayan pulses will at the present stage of electronic technique hardly give occasion to complications even in an unmodified, "classical" apparatus. Using modern electronic equipment the first registration after switching on the current may be taken after say 15 ms, and if one measures as fast as possible errors from convection may be shut out almost beforehand. But when the hot wire is not insulated electrically one should operate below the decomposition voltage of the electrolytic solution, and since the voltage applied to the cell is lower in the modified than in the classical set-up, the first-mentioned set-up is advantageous. Furthermore it is, according to the investigations in [2] and [3], not necessary to measure as fast as possible in order to escape complications from convection. However, it has been shown that one cannot always assume the pulses to be non-faradayan, and the necessity of the modification when "faradayan" delays occur in a set-up with uninsulated wire has been demonstrated. The reasons for trying to escape the electrical insulation round the hot wire have been given in section I.

Furthermore a more detailed explanation than that indicated in [3] has been given of the fact that it is possible to end up with current in the wire and no current in the solution in spite of the "usual" jump condition for the tangential component of the electric field. At the beginning of this section it was shown that non-faradayan pulses will also occur if one uses electrically insulating layers on the electrode plates in "the pure case". This can of course be generalized to apparatuses where the modification is carried out by using an insulating layer round the wire, but from the results concerning the development of non-faradayan pulses obtained in the present work it must be considered highly probable without further analysis that the pulses will not disturb if one - in spite of the difficulties and limitations of that method - modifies by insulating the wire electrically.

V. On the General, Theoretical Foundation of Measurement of the Thermal Conductivity of Liquids

As mentioned at the end of section I: When changing from studying pure (dielectric) liquids to studying liquid mixtures, certain complications in the theoretical foundation of measurement of thermal conductivities will in principle appear.

The foundation of measurements on pure, dielectric liquids was studied in detail in [2], section II, and it is made up of the following

General principles:

The mass balance $\quad \operatorname{div} \rho \vec{v} + \frac{\partial \rho}{\partial t} = 0$

The equations of motion (the momentum balance) $\quad \rho \frac{d}{dt} \vec{v} = - \operatorname{Div} P + \rho \vec{F}$

The energy balance $\quad \frac{d}{dt} \left(\rho \frac{\vec{v}^2}{2} + \rho u \right) = - \operatorname{div} P \cdot \vec{v} + \rho \vec{F} \cdot \vec{v} + \operatorname{div} \vec{j}_u$

The equation for internal energy per unit mass $\quad u = - \frac{p}{\rho} + Ts + \mu$

together with the constitutive equations and definitions of properties of materials such as α and c_p. Especially Fourier's law and Navier–Stoke's law belong to this class of equations. The symbols used are the following:

t = time

$\frac{d}{dt} = \frac{\partial}{\partial t} + \vec{v} \cdot \operatorname{grad}$ (= convective derivative)

ρ = mass density

$\vec{v}$ = velocity

u = internal energy per unit mass

$-P$ = the sum of the viscosity stress tensor and the hydrostatic pressure tensor

$\vec{F}$ = external force per unit mass

$\vec{j}_u$ = flow density of non-mechanical energy transport

p = hydrostatic pressure

T = absolute temperature

s = entropy per unit mass

μ = chemical potential when the mass unit is taken as basis instead of, as in chemistry, the mole

α = volume expansivity

c_p = specific heat at constant pressure

On the basis of this system of equations the following well known equation was derived loc cit

$$\rho\, c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = -\rho\, c_p \vec{v} \cdot \operatorname{grad} T + \operatorname{grad} T \cdot \operatorname{grad} \lambda + \alpha T \frac{dp}{dt} + \Phi, \quad (88)$$

where

λ = thermal conductivity

'∇^2' refers to (cartesian) space coordinates in a coordinate system at rest

'Φ' is an abbreviation introduced for the term owing to internal friction.

As the theoretical foundation - accepted beforehand - in the literature on λ-measurements "the heat flow equation"

$$\rho\, c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = 0 \quad ,$$

is used without*) exceptions.

Since there are no physical principles according to which it can generally be proved that the right-hand side of (88) is equal to 0, it is seen that this foundation is, strictly speaking, an approximation. In [2], section III, this approximation was investigated in detail and found to be valid in the case under consideration.

But even so modest a change as to studying simple, dielectric, binary mixtures with no chemical processes will involve the general as well as the constitutive equations being more complicated. Therefore the question arises whether these complications may turn out to be significant or if they are only of "academic" interest.

In the literature many measured λ-values for liquid mixtures are given. Riedel, for instance, was among the first to undertake in a comprehensive

*) To the author's knowledge.

way such measurements (while working with a refrigeration research institute) using another (steady state) method.

Let us first consider the constitutive equations of non-equilibrium thermodynamics for diffusion transport of chemical components and energy. In section II it was mentioned that if an isotropic mixture of n components is considered, one has n equations (4) for the densities of their diffusion mass flows $\vec{j}_k$:

$$\vec{j}_k = \sum_{r=1}^{n} L_{kr} \vec{K}_r + \gamma_k \operatorname{grad} T, \qquad k = 1 \ldots n, \tag{4}$$

where the $\vec{K}$'s are given by (7). Usually the diffusion flow is defined in the following way: the "barycentric velocity field" $\vec{v}_{bar}$ is introduced by putting

$$\Sigma \rho \vec{v} = (\Sigma \rho) \vec{v}_{bar}, \tag{89}$$

where 'Σ' refers to summation over components. Then one puts

$$\rho_k \vec{v}_k = \rho_k \vec{v}_{bar} + \vec{j}_k, \qquad \text{for every } k, \tag{90}$$

$\vec{v}_{bar}$ is the velocity field which appears in the general balance equations for mass, energy and momentum of mixtures. From (89) and (90) it follows immediately that

$$\Sigma \vec{j}_k = \vec{0} \tag{91}$$

as mentioned in section II. Furthermore it was said there that the equations (4) can be expanded with an equation for the energy diffusion flow density $\vec{j}_u$ (or the entropy flow density). This latter equation has the form

$$\vec{j}_u = \Sigma L' \vec{K}_r + \gamma' \operatorname{grad} T,$$

where L' and γ' are new "phenomenological coefficients".

Taking (7) and (91) into consideration one finds easily from the above that for a dielectric, binary mixture ($k = 1, 2$) "constitutive transport equations" of the following form are valid, μ_1 being the chemical potential of component 1

$$\left.\begin{aligned} \vec{j}_1 &= \alpha \operatorname{grad} \mu_1 + \beta \operatorname{grad} T \\ \vec{j}_u &= \gamma \operatorname{grad} \mu_1 + \delta \operatorname{grad} T \end{aligned}\right\} \qquad (92)$$

$$(\vec{j}_2 = -\vec{j}_1) \quad .$$

α, β, γ and δ we may call 'phenomenological coefficients', although it is more common to call e.g. Tα 'a phenomenological coefficient'.
For pure, dielectric liquids (89) reduces to: the velocity field $\vec{v}$ of the liquid = $\vec{v}_{bar}$ and (90) to: the diffusion mass flow density of the liquid = $\vec{0}$. Therefore (92) reduces simply to the statement *that grad* μ_1 *is proportional* to grad T (with a proportionality factor dependent on p and T) i.e. to

$$\vec{j}_u = -\lambda \operatorname{grad} T \ ,$$

which is "Fourier's law" on the usual form, λ being equal to $\gamma \frac{\beta}{\alpha} - \delta$ and being termed 'the thermal conductivity of the liquid'.

If one wants to speak about "<u>the</u> *thermal conductivity of a binary mixture*" it is seen that the conditions for the energy transport must be specified so *that an interdependence* of grad μ_1 and grad T is given. This is not a discovery by the present author but a well-known fact emphasized in every general treatise on non-equilibrium thermodynamics (see e.g. Haase [9], page 365). In other words the concept of 'thermal conductivity' has now become ambiguous. Since $\mu_1 = \mu_1$ (p, T, x_1), x_1 being the mole fraction of component 1, (92) may be written

$$\left.\begin{aligned} \vec{j}_1 &= a \operatorname{grad} x_1 + b \operatorname{grad} T \\ \vec{j}_u &= c \operatorname{grad} x_1 + d \operatorname{grad} T \ , \end{aligned}\right\} \qquad (93)$$

(where a, b, c and d are new phenomenological coefficients) because we may ignore the dependence of μ_1 on p, or we may *presume mechanical equilibrium* (grad p = $\vec{0}$). In the latter case (93) is valid exactly. As an example of two different meanings, λ_1 and λ_2, of the concept of 'the thermal conductivity of a dielectric, binary mixture' we may give

1) λ_1 = the thermal conductivity in an homogeneous mixture (grad $x_1 = \vec{0}$) :

$$-\lambda_1 = d$$

and

2) λ_2 = the thermal conductivity when no diffusion takes place in a vessel with stationary temperature differences in spite of grad T being $\neq \vec{0}$. i.e. when $\vec{j}_1 = -\vec{j}_2 = \vec{0}$ after thermodiffusion has faded out:

$$-\lambda_2 = d - \frac{cb}{a}$$

λ_1 and λ_2 are evidently not equal.

Let us now investigate the role this ambiguity plays (in principle) for λ-measurements. We shall imagine the λ-measurement of a non reacting, binary, (dielectric) liquid mixture carried out in two different ways. The mixture is poured [1] into the measuring cell of a transient hot wire set-up and [2] into a steady-state apparatus of the "horizontal-lamella" type mentioned in [2], page 62 and indicated at fig. 14a of that report. In the latter apparatus the liquid fills "a gap" between 2 horizontal planes, which are kept at different temperatures. If we imagine that the apparatus functions ideally i.e. that the planes are infinitely extended and that the temperature is absolutely uniformly distributed over each of the planes, it has been shown in [2], page 15, that mechanical equilibrium can be established in spite of the temperature field when the liquid is pure. Furthermore it can be proved that when the lamella is heated from above the mechanical equilibrium is stable. For pure liquids λ may therefore be measured by measuring the flow per unit area of the lamella $\vec{j}_u$ directly and grad T = the difference of the temperature of the planes divided by the thickness of the lamella, when a steady state has been obtained. As to the mixture it is evident from the symmetry that $\vec{j}_1$ and $\vec{j}_2$ must be vertical and that, in the final steady state, we must therefore have $\vec{j}_1 = \vec{j}_2 = \vec{0}$, so that if we proceed as if the liquid were pure the result of the measurement must be

$$\lambda_2 = -\left(d - \frac{cb}{a}\right).$$

This steady-state lamella-method has been widely used - especially in former times - and it is still in use. Let us then imagine that the transient hot wire measurement is carried out on the mixture and that it is also carried out under ideal circumstances i.e. so fast that no appreciable convection and thermodiffusion set in. As the mixture is homogeneous in the initial state, and x_1 can only be altered through diffusion (we assume that no chemical reactions take place), it is seen that during this measurement one has grad $x_1 = \vec{0}$. The result of the measurement will therefore be

$$\lambda_1 = -d$$

In other words: in principle the result is dependent on the measuring procedure and when λ-values for mixtures are given in the literature this procedure should, strictly speaking, always be mentioned if it turns out that the *difference* between λ_1 and λ_2 is *significant*.

The deviation of λ in the two cases described is

$$p = 10^2 \frac{\lambda_1 - \lambda_2}{\lambda_1} \% = -10^2 \cdot \frac{cb}{a\lambda_1} \%$$

In practice, the coefficients a, b, c and d are not used, but different authors use different combinations of T, p, x_1 and the coefficients mentioned. Meixner and Reik [12], page 452, e.g. use the "diffusion coefficient at constant temperature D_{12}" and the "thermodiffusion factor α", the definitions of which are given loc cit. Meixner and Reik of course do not treat measuring problems in their general, theoretical treatise - as done here - but incidentally in another connection they calculate (on page 454) just what we need here. From their calculations is seen that for an ideal binary, gaseous mixture one has

$$p \simeq 1.5 \%$$

and this is not negligible when the accuracy of modern (and future) measurements for basic studies mentioned in [2], section VII is taken into consideration. As the example concerns an ideal mixture, one may expect that p may in some cases be more than 1.5 %. At highly exact calculations concerning mixtures of gases, the question therefore arises as to what method has been used for the determination of the λ-value. If the method is not known, it is not known what is the quantity that has been called 'λ' and for which the value has been inserted in the equations of the actual problem.

For liquid, dielectric mixtures, however, it can probably be established that problems of this kind are quite negligible in most cases, i.e. p becomes extremely small (Examples of values will be given below). As to measurements by the transient hot-wire method it may then be assumed that the uncertainty due to the possible establishment of grad x-fields during the period of measurement is disposed of, or in other words that in practice there is no ambiguously defined "compromise" between λ_1 and λ_2 that may be accidentally determined.

In the above considerations it has been tacitly assumed that the necessary generalization of the equation for the internal energy per unit mass given on

page 67, when passing to study dielectric mixtures, is of no importance for the transient measurement. This generalization will, strictly speaking, give rise to extra terms in the "heat flow equation" (the energy balance) which can, however, no doubt be neglected in measurements involving only small concentration differences.

If one passes from studying dielectric mixtures to studying electrolytic solutions the energy balance will become further complicated by new "source--terms", and the constitutive equations are also altered. Strictly speaking a new analysis should therefore be undertaken. But it would carry us too far to delve into that problem. Suffice it here to refer to the good agreement between λ-values obtained by the author's measurements by his modification of the transient hot-wire method, ignoring the complications, and measurements obtained by other researchers by other methods. Furthermore, as soon as the current pulse has faded out the electric field in the liquid has vanished and there are no "source terms" owing to the solution being electrolytic. So the thermoelectric disturbances of the T field cease quickly in the modified apparatus.

We shall now investigate what can be said about the values of p for some binary, liquid mixtures. For diluted solutions - obviously aqueous - Meixner and Reik [12], pp. 453-454, give the following values

$$\lambda \simeq 10^{-3} \frac{\text{cal}}{\text{cm sec } {}^{o}\text{C}}, \quad D_{12} \simeq 10^{-5} \frac{\text{cm}^2}{\text{sec}}, \quad \rho \simeq 1 \frac{\text{g}}{\text{cm}^3},$$

$$T \simeq 300^{o}\text{K}, \quad \left(\frac{\partial \mu}{\partial \gamma}\right)_{T,p} \simeq 5 \frac{\text{cal}}{\text{g}}, \quad \gamma \simeq \frac{1}{10}$$

$$a^2 < 6 \cdot 10^4$$

where γ = the mass fraction of the dissolved component, μ = its chemical potential and ρ = the mass density of the solution. The limit given for a is found by theoretical considerations. Measured values of $|a|$ are said to lie between 1 and 10. If $|\Delta\lambda|$ is the numerical value of the difference between the two λ-values the formula given by Meixner and Reik reads

$$|\Delta\lambda| = \frac{\rho\gamma^2(1-\gamma)}{T}\left(\frac{\partial \mu}{\partial \gamma}\right)_{T,p} a^2 D_{12}.$$

If one uses a high value of $|a|$, e.g. 10, it is found from this formula and the above values that

$p \simeq 1.5 \cdot 10^{-1}$ 0/00

which, within the measuring accuracy possible, is completely negligible. Since p is proportional to a^2, p is thus always negligible for solutions as those considered here.

Now these evaluations - valid for binary mixtures only - refer to organic aqueous solutions, as e.g. an aqueous solution of sugar. Since it would be a very comprehensive study to try to treat general multicomponent systems with charged components we shall stop the investigation here making what might be called 'a plausible guess', namely that the limits of p will be about the same as just found for binary mixtures with uncharged components for all the electrolytic solutions studied in the author's experimental work. But as the author has been interested in the theory of the method in general, i.e. also in its application to dielectric liquids (cf [2]) the following might finally be pointed out roughly: When studying binary mixtures of organic liquids the values used above for the calculation of p will change (at any rate the values of λ and ρ). On pages 309, 404, 405 and 406 Haase [9] gives examples of data that make it possible to estimate p as in the preceding case. If the mixtures are assumed ideal, one further knows $(\frac{\partial \mu}{\partial \gamma})_{T,p}$, and it will be found as before that p is negligible. But if an example far from ideality is desired, an homogeneous phase may be considered that is close to a temperature critical for the miscibility of the components, T_{crit}. When $T \to T_{crit}$, $(\frac{\partial \mu}{\partial \gamma})_{T,p}$ will $\to 0$. This does not mean, however, that p will necessarily $\to 0$ because Haase gives examples where $T \to T_{crit}$ results in other factors ("s" and "D") in the expression used by him $\to \infty$ and 0 (respectively). In other words: close to T_{crit} it is hardly possible to say anything about the value of p and exceptions from the result that p is negligible may occur.

References

[1] Alas, Chiquillo, Messung der relativen Wärmeleitfähigkeit wässriger Salzlösungen nach einem instationären Hitzdrahtverfahren. Dissertation Eidgenössische Technische Hochschule Nr. 3955 (Juris Verlag, Zürich, 1967) 77 pp.

[2] Baruël, P., On Transient Hot-Wire Determination of the Thermal Conductivity of Pure, Dielectric Liquids. Risø Report No. 263 (1972) 65 pp.

[3] Baruël, P., On Transient Hot-Wire Measurement of the Thermal Conductivity of Electrolytic Solutions. Risø Report No. 264 (1972) 65 pp.

[4] Born, Max. and Wolf, Emil., Principles of Optics. 2nd edition. (Pergamon Press, London, 1964) 808 pp.

[5] de Groot, S.R. and Mazur, P., Non-Equilibrium Thermodynamics (North Holland, Amsterdam, 1962) 510 pp.

[6] Delahay, P., Double Layer and Electrode Kinetics. (Interscience, New York, 1965) 321 pp.

[7] Eucken, A. and Englert, H., Z. ges. Kälteind. 45 (1938) 109-113.

[8] Forker, W., Elektrochemische Kinetik (Akademie-Verlag, Berlin, 1966) 176 pp.

[9] Haase, R., Thermodynamik der irreversiblen Prozesse (Steinkopf Verlag, Darmstadt, 1963) 552 pp.

[10] Harned, H.S. and Owen, B.B., The Physical Chemistry of Electrolytic Solutions, 3rd edition (Reinhold, 1958) 803 pp.

[11] Macdonald, J.R. and Barlow, C.A., J. Chem. Phys. 36 (1962) 3062-80.

[12] Meixner, I. and Reik, H.G., Thermodynamik der irreversiblen Prozesse. In: S. Flügge (editor), Handbuch der Physik, Bd. III/2 (Springer Verlag, Berlin, 1959).

[13] Stålhane, B. and Pyk, S., Tekn. Tidsskrift A61 (1931) 389-393.

[14] Thon, N., L'électrolyse et la polarisation électrolytique (Hermann & C^{ie}, Paris, 1934) 34 pp.

[15] Tye, R.P. (editor), Thermal Conductivity. (Academic Press, London, 1969) Vol. 1-2.

[16] van der Held, E.F.M. and van Drunen, F.G., Physica 15 (1949) 865-881.

[17] van der Held, E.F.M., Hardebol, J., and Kalshoven, J., Physica 19 (1953) 208-216.